## (12) UK Patent Application (19) GB (11) 2 290 629 (13) A

(43) Date of A Publication 03.01.1996

- (21) Application No 9512661.1
- (22) Date of Filing 21.06.1995
- **Priority Data** 
  - (31) 06143659 06298712
- (32) 24.06.1994 01.12.1994
- (33) JP

(71) Applicant(s)

Alps Electric Co Ltd

(Incorporated in Japan)

- 1-7 Yukigaya, Otsuka-cho, Ota-ku, Tokyo 145, Japan
- (72) Inventor(s)

Munemitsu Abe

Yorihiko Sasaki

Mitsuru Kano

Yoshihiko Ishitaka

Yumiko Sato

Tomomasa Takatsuka

- (51) INT CL<sup>6</sup> G02F 1/1337, B29C 59/02 // B29K 31:00, B29L 31:00
- (52) UK CL (Edition O)

**G2F** FCT F23E F24T F25F

**B5A** ANA AT1P A1R314C1F A1R314C1S A1R413 A2A1

A2F26 A2X A20T1

(56) Documents Cited

DE 004213802 A **US 5280375 A** 

Patent Abstracts of Japan Section P:P-P-177 Vol. 7

No.42 &JP 57192926

(58) Field of Search

UK CL (Edition N ) G2F FCT

INT CL<sup>6</sup> G02F 1/1337

ONLINE: EDOC WPI PAJ

(74) Agent and/or Address for Service

Saunders & Dolleymore

9 Rickmansworth Road, WATFORD, Herts, WD1 7HE,

United Kingdom

## (54) Liquid crystal alignment film

(57) The surface shape of an alignment film 116 for a liquid crystal device is formed by pressing or stamping with a die 110. The surface shape thus produced takes the form of an irregular pattern with the pitch of the irregularities in one direction being different from the pitch of the irregularities in another direction. Such an arrangement results in a plurality of alignment domains differing in pre-tilt angle. The die is produced by two stamping processes imposing two different patterns of irregularities on the die. The die comprises in order a press base body of rigid material, an elastic member and a sheet like die member.

FIG. 17

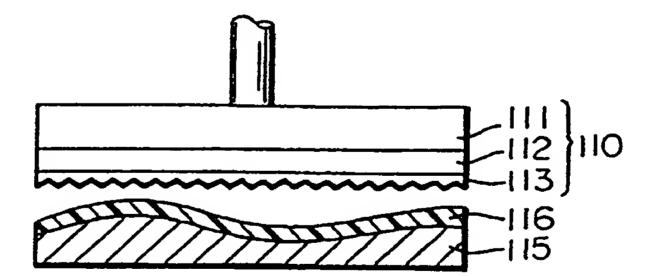


FIG. 1

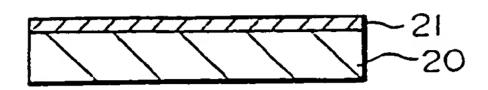
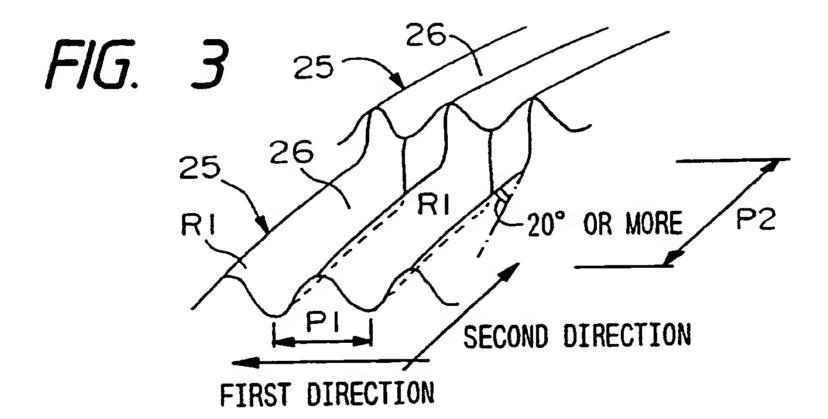


FIG. 28 23 29 27 R2 R2 20



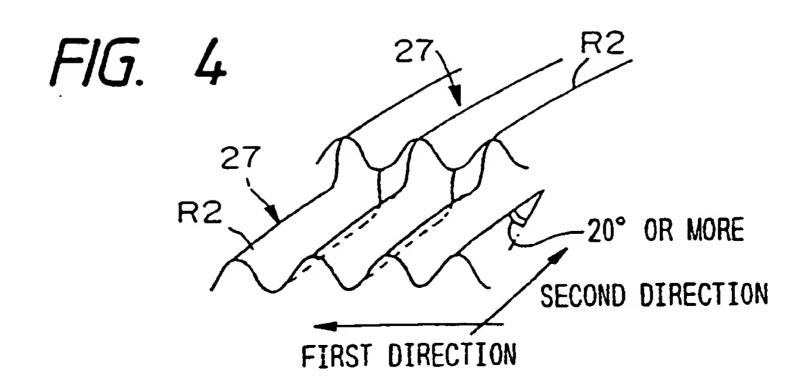


FIG. 5

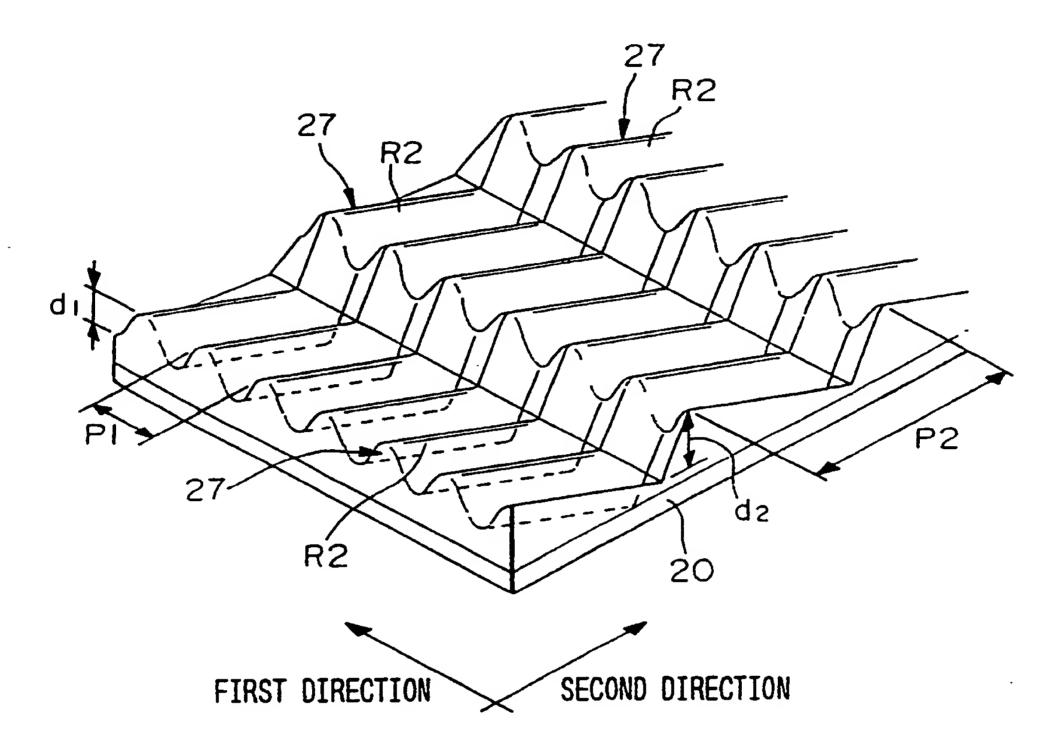


FIG. 6

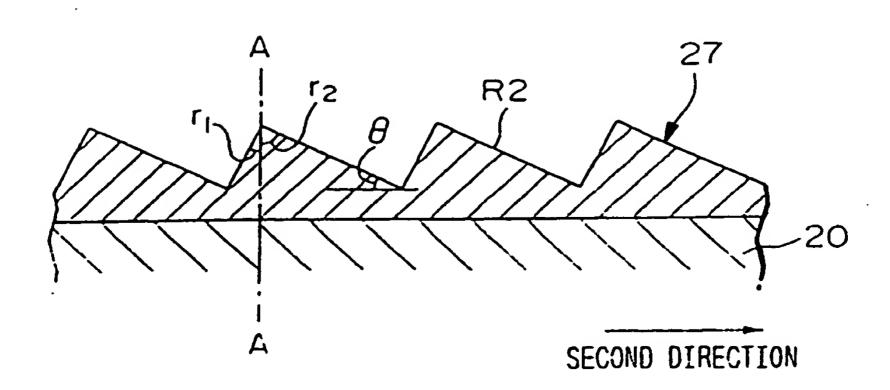


FIG. 7

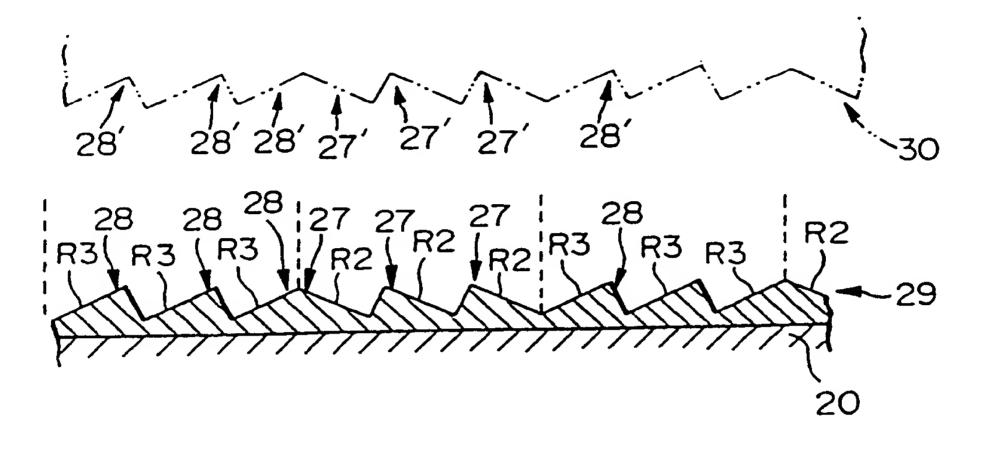
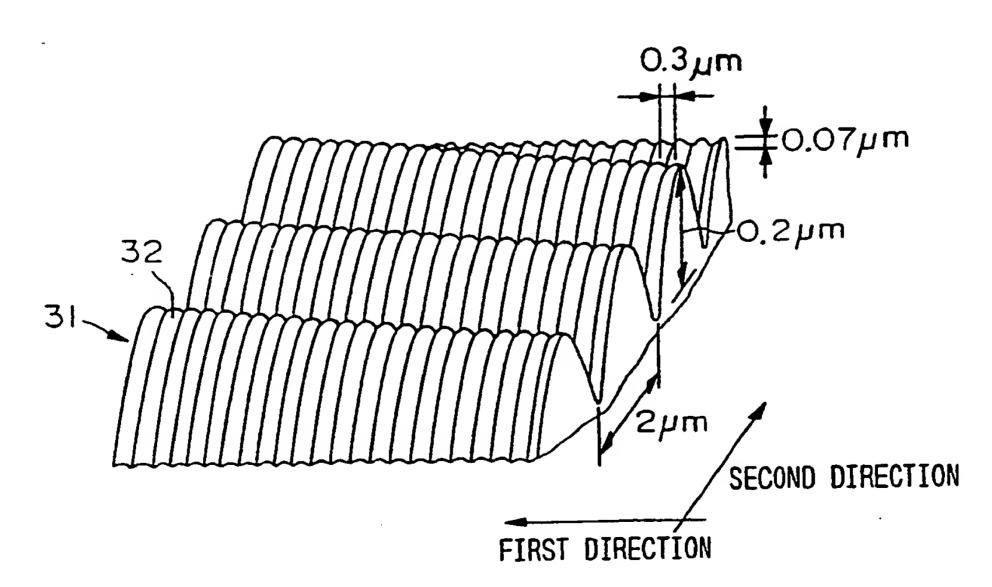
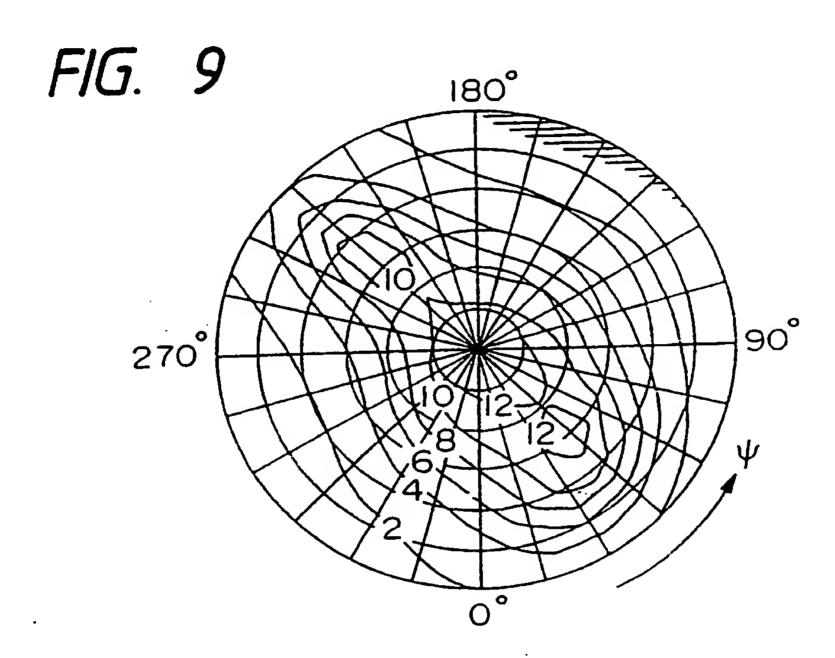
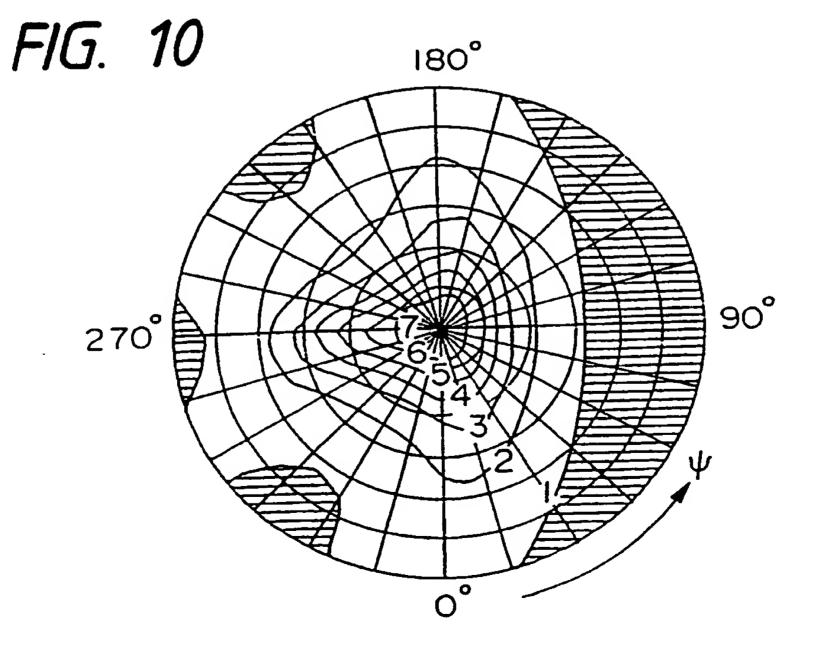


FIG. 8







\*\*\*

FIG. 11A	18 -15 -14 -14 -14
F/G. 11B	24 22 19 15
FIG. 11C	15 14 34
FIG. 11D	33 15) 34
FIG. 11E	$\begin{array}{c} 15 \\ 14 \end{array}$
FIG. 11F	35
F/G. 11G	77777777777777-35
FIG. 12	

22 24 22 24

FIG. 13A PRIOR ART FIG. 13B PRIOR ART FIG. 13C PRIOR ART FIG. 13D PRIOR ART FIG. 13E PRIOR ART FIG. 13F PRIOR ART

FIG. 13G

PRIOR ART

FIG. 14A PRIOR ART FIG. 14B PRIOR ART FIG. 14C PRIOR ART FIG. 14D PRIOR ART PRIOR ART 10' FIG. 14G PRIOR ART 17-5

FIG. 15 PRIOR ART

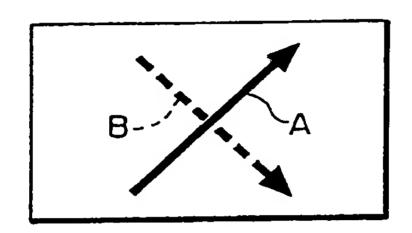
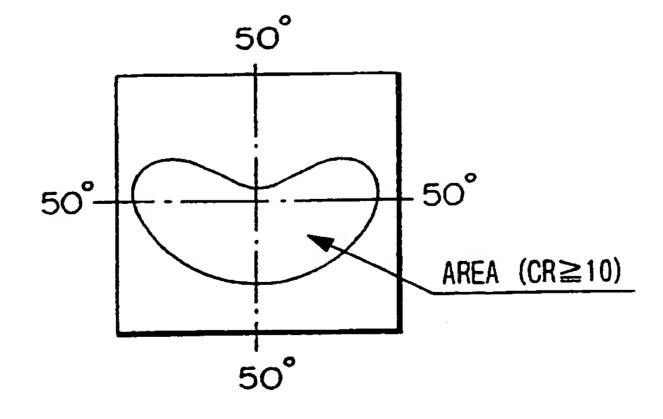
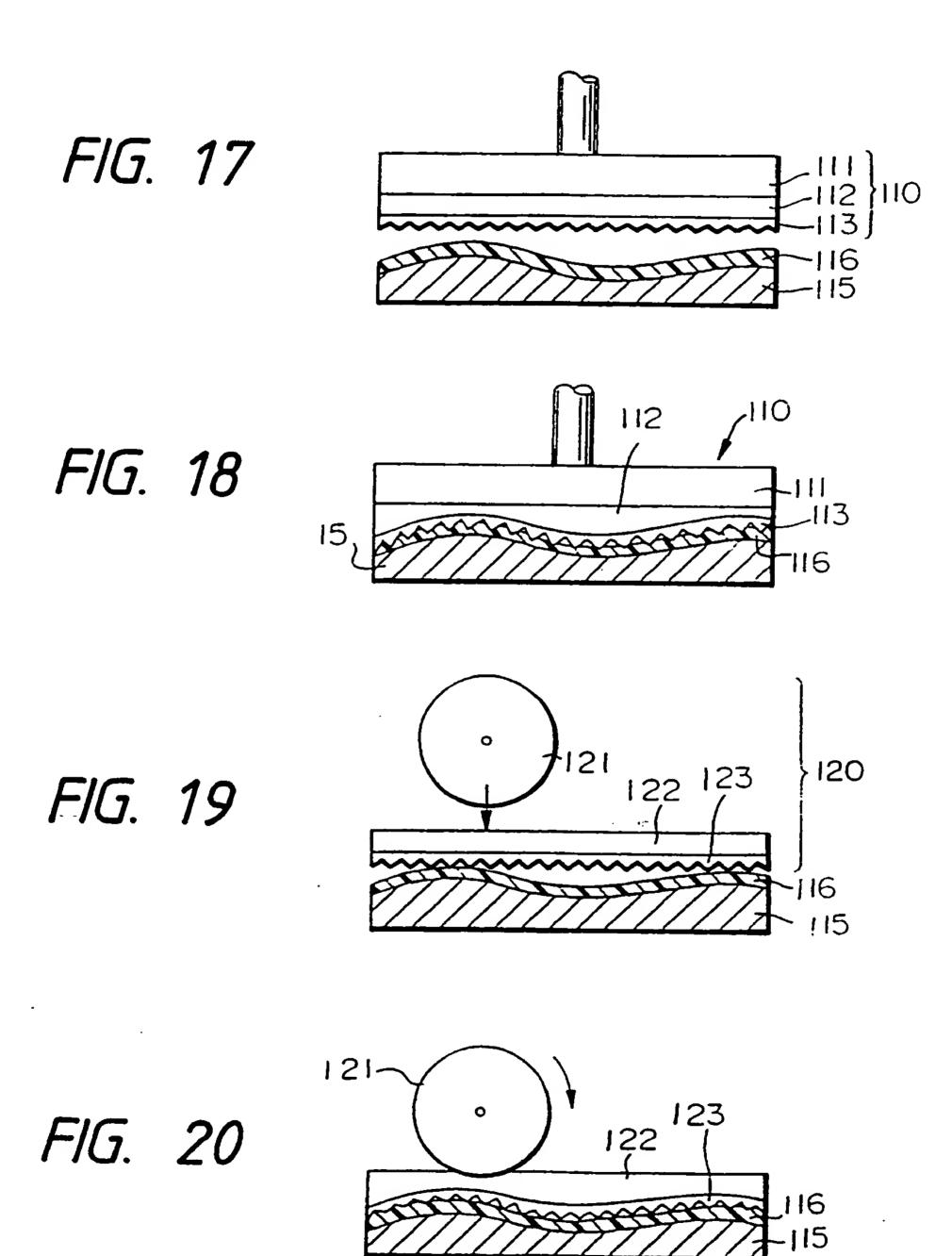


FIG. 16 PRIOR ART





erentur 230 eennenna

FIG. 21

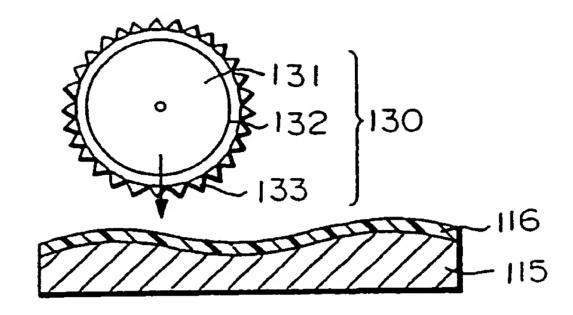


FIG. 22

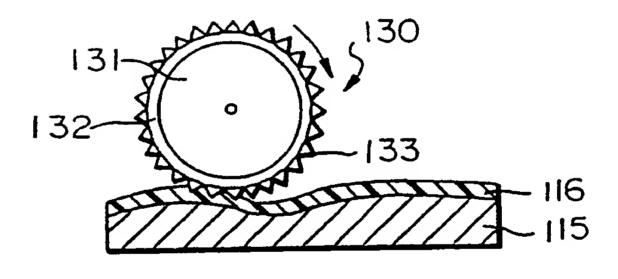


FIG. 23

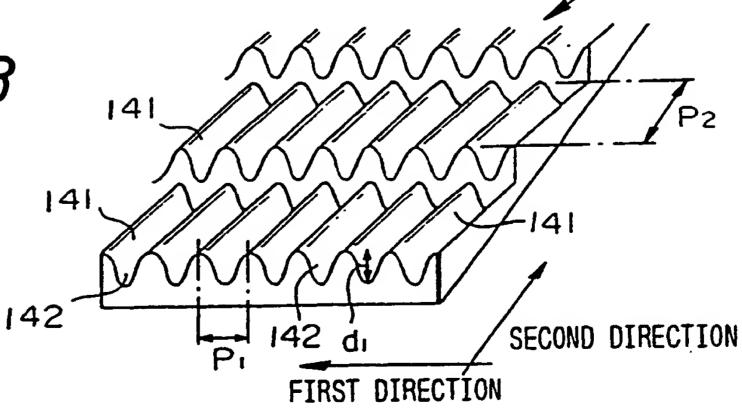


FIG. 24A

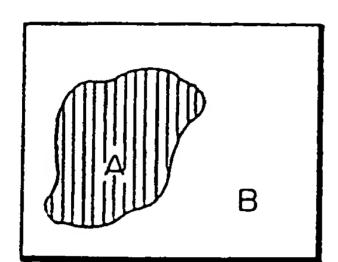


FIG. 24B

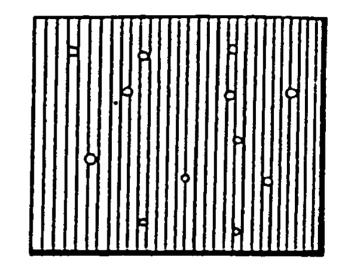


FIG. 25A PRIOR ART

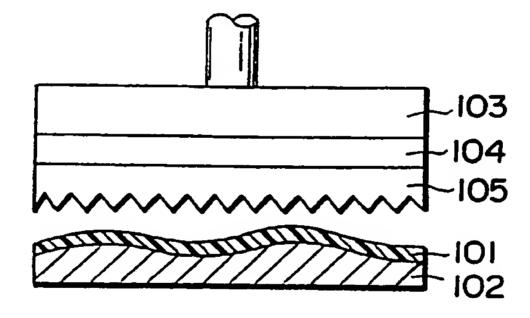
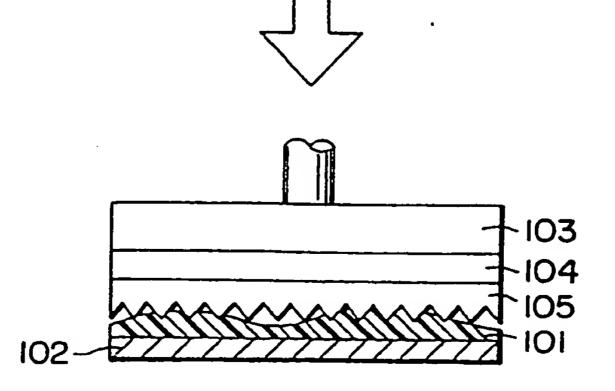


FIG. 25B PRIOR ART



LIQUID CRYSTAL ELEMENT AND ITS MANUFACTURE, FORMATION OF
ALIGNMENT FILM FOR LIQUID CRYSTAL ELEMENT, STAMPING DIE FOR
FORMING ALIGNMENT FILM AND ITS MANUFACTURE, AND APPARATUS
FOR STAMPING IRREGULAR PATTERN ON ALIGNMENT FILM

The present invention relates to a technique of forming a liquid crystal element exhibiting a wide visual field angle, and particularly to a liquid crystal element having an alignment film capable of realizing a wide visual field angle and its manufacture, and a stamping die for forming an alignment film for a liquid crystal element and its manufacture.

The present invention further relates to an irregular pattern stamping apparatus suitably used for forming the above-described alignment film on a liquid crystal substrate.

A liquid crystal element of a thin film transistor drive type has been extensively known as a high quality image thin type display capable of obtaining a high response speed and full color display. The liquid crystal element of this type, however, has a problem that a visual field angle is

narrow.

Conventionally, in the liquid crystal element of this type, there has been known a technique of dividing alignments of liquid crystal molecules for each pixel for widening a visual field angle. Specifically, according to the above-described technique, each dot of R, G and B constituting a pixel has domains different from each other in the rising alignment of liquid crystal molecules when a voltage is applied. In such an alignment division structure, generally, each dot is divided into two parts, and the divided parts are subjected to different alignment treatments.

This alignment division technique is effective to soften a rapid and asymmetric change in contrast in the vertical direction which has been regarded as a problem in the liquid crystal element of a thin film transistor drive type, and to enlarge a domain in which the reversal of an intermediate tone is not generated. Consequently, this technique has a possibility of providing a liquid crystal element having a wide visual field angle.

One example of a prior art method of manufacturing a liquid crystal element having an alignment division structure will be described below.

As shown in Fig. 13A, an alignment film preliminary

layer 2 is formed on the upper surface of a substrate 1, and as shown in Fig. 13B, the alignment film preliminary layer 2 is subjected to a first rubbing treatment.

The rubbing treatment is carried out by a method wherein the upper surface of the alignment film preliminary layer 2 is rubbed with a roller 6 having a rubbing cloth attached around the outer peripheral portion thereof.

Next, as shown in Fig. 13C, a photoresist 3 is applied on the upper surface of the alignment—film preliminary layer 2 thus rubbed, and a resist pattern is developed as shown in Fig. 13D. As shown in Fig. 13E, the second rubbing treatment is carried out on the alignment—film preliminary layer 2 formed with the resist 3 in the direction reversed to the first rubbing treatment. After that, the resist 3 is removed, to thus obtain the substrate 1 formed with an alignment—film 5 shown in Fig. 13F.

至

-

27

2

Fig. 13G shows one construction example of a liquid crystal element using the alignment film 5 having the above structure. In this structure, liquid crystal molecules 7 are sealed between a substrate 1 formed with an alignment film 5 on the color filter side and a substrate 1' formed with an alignment film 5' on the transistor side. The liquid crystal molecules on the alignment film 5 side (on the color filter side) and the liquid crystal molecules on the

- 3 -

alignment film 5' side (on the thin film transistor side) are set to be at a pretilt angle so as to be parallel to each other, by alignment control of the alignment films 5 and 5'.

The above-described prior art method, however, has the following disadvantage: Namely, in the second rubbing treatment performed by way of the resist 3 after the first rubbing treatment performed over the whole surface, the rubbing must be carried out in the reversed direction using opening portions each having a size being half that of a fine dot. Moreover, in the second rubbing treatment, a large area mask must be used. Consequently, such a rubbing treatment is difficult to be practically realized.

Another problem is that when a photoresist is applied on the rubbing surface and developed, the alignment film tends to be dissolved by an alkali component contained in a development solution, and in this case, even when the alignment film is not perfectly dissolved, at least part of the surface of the film is liable to be altered, thus failing to realize the stable alignment state by the rubbing treatment.

A further problem arises, in which since the remaining photoresist must be removed, the alignment—film tends to be further damaged by the removal of the remaining photoresist,

•

and consequently, the initial rubbing state is difficult to be kept, thus failing to ensure stable alignment division over a wide area.

In recent years, a method capable of practically solving the above-described prior art disadvantages has been proposed. Such a method will be described below with reference to the drawings.

First, as shown in Fig. 14A, a low pretilt angle alignment film 11 made of an inorganic material is formed on a substrate 10; a high pretilt angle alignment film 12 is laminated thereon as shown in Fig. 14B; and a photoresist 13 is laminated thereon as shown in Fig. 14C. Subsequently, as shown in Fig. 14D, the photoresist 13 is developed and the high pretilt angle alignment film 12 is etched, followed by the rubbing treatment using a roller 16 as shown in Fig. 14E, thus manufacturing an alignment film.

. 🚓

حثئد

E

-24

K

3

In this method, since only one rubbing treatment is required and further the high pretilt angle alignment film 12 is subjected to the rubbing treatment after removal of the resist, the alignment state can be stabilized. Moreover, since the low pretilt angle alignment film 11 at the first layer is made of an inorganic material, it becomes possible to reduce the influence of the photoresist on the development solution, and hence to obtain a stable alignment film.

Fig. 14F shows one construction example of the liquid crystal element using the alignment film having such a structure, wherein liquid crystal molecules 17 are sealed between a substrate 10 and low and high pretilt angle alignment films 11, 12 on the color filter side, and a substrate 10 and low and high pretilt angle alignment films 11', 12' on the thin film transistor side. The pretilt angle of liquid crystal on the alignment film on the color filter side and the pretilt angle of liquid crystal molecules on the alignment film on the thin film transistor side are set to be different from each other by alignment control of the low pretilt angle alignment films 11, 11, and the high pretilt angle alignment films 12, 12'.

As described above, an orientation film for orienting liquid crystal in a specified direction is formed within a substrate of a liquid crystal element. The alignment film has been generally obtained by rubbing a rubbing cloth on the surface of an alignment film preliminary layer (resin film) for giving a specified alignment. In the rubbing treatment, dust is generated and thereby the surface of the alignment film tends to be contaminated by the dust, thus harming the alignment of the alignment film.

To cope with the problems, the present inventors has examined a technique of forming an alignment film by a

stamp method.

An alignment film on a substrate of a liquid crystal element is formed on the surface of a substrate main body being high in rigidity such as glass, generally, to a thickness of 1  $\mu$ m or less for lowering the drive voltage of the liquid crystal element; accordingly, a preferable irregular pattern cannot be formed only by pressing of a die thereon just as the formation of an irregular pattern on a soft and thick plastic film.

1

77

74.3

-

.....

-3°

-

Specifically, for forming an irregular pattern on the surface of a thin alignment film, it is required to accurately press a die on a resin made alignment film preliminary layer at a uniform pressure. For this purpose, in the case of pressing using a press, it is required to enhance the flatness and parallelism of a die plate and die set of the press, and to equalize the in-plane pressure distribution upon pressing of the die onto the alignment film preliminary layer.

The method of manufacturing a liquid crystal element having the prior art structure requires a photolithography process, tending to complicate the whole manufacturing process, to deteriorate productivity, and to increase a manufacturing cost.

In the prior art manufacturing method, moreover,

residue in the photolithography process tends to be contained in an alignment film, thus causing a fear in reducing the yield of products.

Additionally, in the rubbing process, an alignment film preliminary layer is rubbed with a rubbing cloth and thereby dust is generated, while a clean room is required for masking by photolithography, and consequently, the management of the whole process is complicated, and it becomes difficult to keep high quality through the whole process.

In the prior art method described with reference to Fig. 13, the resist 3 is formed after the first rubbing treatment and openings are formed by patterning of the resist, after which the alignment film 2 initially rubbed is partially rubbed again in another direction over the openings of the resist 3 in the state that part of the alignment film 2 initially rubbed is protected. As a result, since the domains of the resist 3 in openings are twice rubbed, portions of the resist 3 near the openings cannot be rubbed at a high accuracy. In this rubbing treatment, the treated magnitude of a pixel is limited to about 100  $\mu$ m $\times$ 100  $\mu$ m.

Fig. 15 is a plan view showing the rubbing directions of alignment films in one example of a liquid crystal element in which the rubbing direction of the alignment

film on the color filter side is different from the rubbing direction of the alignment film on the thin film transistor side, wherein the rubbing direction A is perpendicular to the rubbing direction B.

Incidentally, the liquid crystal element having such a structure has a visual field angle characteristic shown in Fig. 16, and has a disadvantage that the vidual field angle is narrow in a specified direction. The visual field angle characteristic shown in Fig. 16 has an area of CR ≥10.

 $\equiv$ 

Ξ,

2

Here, the wording "CR" means "contrast", and is defined in the following equation, for a normally white type liquid crystal (white display upon applying of no voltage, and black display upon applying of voltage).

CR = (transmissivity upon applying of no voltage)/(transmissivity upon applying of voltage)

CR is also defined by the following equation, for a normally black type liquid crystal (black display upon applying of no voltage, and white display upon applying of voltage).

CR = (transmissivity upon applying of
voltage)/(transmissivity upon applying of no voltage)

In the liquid crystal element in which the combination of the rubbing direction of an alignment film on the color filter side and the rubbing direction of an alignment film

- 9 -

on the thin film transistor side is different for each pixel of each thin film transistor, a substrate including one alignment film and another substrate including another alignment film are accurately positioned and joined to each other while eliminating the generation of any error in the order of pixel unit, and liquid crystal is sealed therebetween. At this time, if the above-described positioning accuracy is only slightly poor, it becomes difficult to obtain a desirable alignment of liquid crystal.

Incidentally, the twisting angle of an STN (Super Twisted Nematic) liquid crystal is generally in the range of from 180 to 240°, and it may be considered that the visual field angle can be enlarged by increasing the twisting angle.

However, to obtain the twisting angle of 240° in the STN liquid crystal, the pretilt angle of liquid crystal molecules must be 6° or more, and in the alignment film subjected to the prior art rubbing treatment using a rubbing cloth, it is difficult to stably form the pretilt angle of 6° or more.

A method has been known of forming projecting portions at a tilting angle of 6° or more by a special evaporation called the tilting evaporation thereby realizing a high pretilt angle; however, this method is high in manufacturing

cost, and is not suitable for mass-production.

Incidentally, the present inventors have found that even when a high flatness stamping die for forming an alignment film is pressed on an alignment film preliminary layer, the surface shape of the stamping die is sometimes not perfectly stamped on the alignment film preliminary layer.

The reason for this is that as shown in Fig. 25A, a transparent substrate 102 made of glass formed with an alignment film preliminary layer 101 has generally fine waviness, irregularities or tilting, and thereby it is uneven in its thickness, as a result of which even when it is sufficiently subjected to surface finish such as grinding, slight waviness, irregularities or tilting remain on the upper surface of the substrate 102.

4

\*\*

3.

\*

Specifically, when the pressing is performed using a stamping apparatus including a press base body 103 having a high flatness, a sheet-like elastic member 104 stuck on the press base body 103 and a plate-like die member 105, a domain where the die member 105 is not pressed on the alignment film preliminary layer 101 as shown in Fig. 25B is generated. This domain leads to a failure in alignment, thus causing a failure in display of the liquid crystal display.

Moreover, in the case where an irregular pattern is

- 11 -

formed on the alignment film preliminary layer 101 by the die member 105 and then the die member 105 is separated from the alignment film preliminary layer 101, if the die member 105 and the alignment film preliminary layer are made of materials liable to be easily bonded to each other, part of the alignment film preliminary layer 101 is peeled and stuck on the surface of the die member 105, to damage part of the alignment film, thus causing unevenness in display. In addition, since the alignment film preliminary layer is generally made of aromatic polyamide, the above-described problem in peeling of the alignment film is significantly enlarged in the case where the die member 105 is made of nickel.

## SUMMARY OF THE INVENTION

• •

In view of the foregoing,

an object of the present invention is to provide a liquid crystal element and its manufacture; formation of an alignment film for a liquid crystal; and a stamping die for forming an alignment film for a liquid crystal element and its manufacture, wherein an alignment film having a plurality of uniform alignment domains can be manufactured and thereby a liquid crystal display element having a wide visual field angle can be obtained.

Another object of the present invention is to provide a stamping apparatus enabling smooth stamping of an irregular pattern and preventing the peeling of part of an alignment film preliminary layer upon separation from a stamping die thereby eliminating the generation of peeling failure, even when an alignment—film is formed on a substrate having slight tilting, irregularities or waviness.

To achieve the above object, according to a preferred mode as described in claim 1, there is provided a liquid crystal element comprising:

¥...

-

Z .

a pair of substrates disposed so as to face to each other, and having respective alignment films on the facing surfaces thereof; and

liquid crystal held between said substrates;

wherein a surface shape of said alignment film formed on at least one of said substrates is formed by pressing of a die, and

said alignment film formed with the surface shape by pressing of the die has a plurality of uniform alignment domains which are different from each other in the emergent direction or emergent magnitude of a pretilt angle of liquid crystal within an effective display plane.

According to a preferred mode as described in claim 2, there is provided a liquid crystal element defined in the

- 13 -

preferred mode as described in claim 1, wherein said alignment film formed on one of said substrates and having a plurality of said uniform alignment: domains has two directional uniform alignment domains in which the emergent directions of the pretilt angle of liquid crystal are approximately parallel to each other, and said alignment film formed on the other of said substrates has a pretilt angle lower than said pretilt angle in one of said substrates.

According to a preferred mode as described in claim 3, there is provided a liquid crystal element defined in the preferred mode as described in claim 1 or 2, wherein the surface shape of said alignment—film is formed by collection of a plurality of projecting portions having tilting surfaces, and said tilting surfaces of said projecting portions function as a means of adjusting the pretilt angle of liquid crystal.

According to a preferred mode as described in claim 4, there is provided a liquid crystal element defined in the preferred mode as described in any of claims 1 to 3, one uniform alignment domain having an emergent direction or emergent magnitude of a pretilt angle of liquid crystal is formed by the collection of first projecting portions having tilting surfaces extending at a tilting angle, and the other

- 14 -

uniform alignment domain having an emergent direction or emergent magnitude of a pretilt angle different from that in said one uniform alignment domain is formed by collection of a plurality of second projecting portions having tilting surfaces extending at an angle different from that of said tilting surfaces of said first projecting portions.

According to a preferred mode as described in claim 5, there is provided a liquid crystal element defined in the preferred mode as described in any of claims 1 to 4, wherein the surface shape of an alignment film is formed by collection of projecting portions having tilting surfaces, and the tilting angle of the tilting surfaces of said projecting portions formed on the surface of said alignment film is specified at 6° or more.

13

35

-3

-

3

According to a preferred mode as described in claim 6, there is provided a method of manufacturing a liquid crystal element having liquid crystal held between a pair of substrates, said substrates being disposed so as to face to each other and having respective alignment films on the facing surfaces thereof; comprising:

an alignment film preliminary layer forming process of forming an alignment film preliminary layer on the surface of each of said substrates; and

a shape imparting process of pressing a die capable of

forming a plurality of uniform alignment domains different from each other in an emergent direction or emergent magnitude of a pretilt angle of liquid crystal within an effective display plane on the surface of said substrate, on the surface of at least one of said alignment film preliminary layer.

According to a preferred mode as described in claim 7, there is provided a method of manufacturing a liquid crystal element having liquid crystal held between a pair of substrates, said substrates being disposed so as to face to each other and having respective alignment films on the facing surfaces thereof; comprising:

an alignment film preliminary layer forming process of forming an alignment film preliminary layer on the surface of each of said substrates; and

a first shape imparting process of pressing a die capable of forming uniform alignment domains nearly equal to each other in an emergent direction or emergent magnitude of a pretilt angle of liquid crystal within an effective display plane on the surface of said substrate, on the surface of at least one of said alignment film preliminary layer; and

a second shape imparting process of pressing a die capable of forming uniform alignment domains different in

the emergent direction of the pretilt angle from those obtained in said first shape forming process, on the surface of said alignment film preliminary layer.

According to a preferred mode as described in claim 8, there is provided a method of manufacturing a liquid crystal element defined in the preferred mode as described in claim 6 or 7, which further comprises a shape imparting process of pressing said die on one of said alignment film preliminary layers, and a process of pressing an approximately cylindrical roller formed at least on the surface with an elastic body on the other of said alignment film preliminary layers.

برياب. د الشهر

1

\*\*\*

\$

7.

According to a preferred mode as described in claim 9, there is provided a method of manufacturing a liquid crystal element defined in the preferred mode as described in any of claims 6 to 8, wherein said uniform alignment domains are formed using a stamping die in which a plurality of projecting portions having tilting surfaces are formed on the surface and the tilting angle of said tilting surfaces of said projecting portions is specified at 6° or more.

According to a preferred mode as described in claim 10, there is provided a method of manufacturing a liquid crystal element defined in the preferred mode as described in any of claims 6 to 9, wherein said shape imparting process is

carried out using a die on the surface of which a plurality of first portions each forming one uniform alignment domain and a plurality of second portions each forming the other uniform alignment domain are formed, said first portion being constituted of collection of a plurality of projecting portions with tilting surfaces having the same tilting direction and the same tilting angle, and said second portion being constituted of a plurality of projecting portions with tilting surfaces having a tilting direction and a tilting angle different from said tilting direction and said tilting angle of said first portion.

According to a preferred mode as described in claim 11, there is provided a stamping die for forming an alignment film for a liquid crystal element, which is pressed on the surface of a resin made alignment film preliminary layer formed on a substrate for a liquid crystal element for forming a plurality of projecting portions on the surface of said alignment film preliminary layer, comprising:

irregularities repeatedly formed on the surface of said stamping die along a first direction; and

irregularities repeatedly formed on the surface of said stamping die along a second direction crossing said first direction,

wherein the tilting direction of said tilting surfaces

formed by said irregularities are specified for each of a plurality of divided domains formed on the surface of said stamping die.

According to a preferred mode as described in claim 12, there is provided a stamping die for forming an alignment film for a liquid crystal element defined in the preferred mode as described in claim 11, wherein the tilting angle of said tilting surfaces of said projecting portions formed on the surface of said stamping die is specified at 6° or more.

According to a preferred mode as described in claim 13, there is provided a stamping die for forming an alignment film for a liquid crystal element defined in the preferred mode as described in claim 11 or 12, wherein said divided domain of said stamping die is equivalent to one of said projecting portions formed on said stamping die.

- <del>- -</del>

According to a preferred mode as described in claim 14, there is provided a method of manufacturing astamping die for forming an alignment film for a liquid crystal element comprising:

a first heating process of heating a stamping film made of a thermoplastic ultraviolet ray hardening resin formed on a substrate;

a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of

- 19 -

irregularities are repeatedly formed along an optional direction, on said stamping film; a ultraviolet ray emitting process of disposing a mask formed with opening portions at suitable intervals, and emitting ultraviolet rays to said stamping film through said mask; a second heating process of heating said stamping film after said ultraviolet ray emitting process; a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along a direction different from said optional direction in said first stamping process, on said stamping film; and a process of pressing said stamping die on said stamping film after said second stamping process, thereby stamping the surface shape of said stamping film on said stamping die. According to a preferred mode as described in claim 15, there is provided a method of forming an alignment film for a liquid crystal element, comprising: a first heating process of heating an alignment film preliminary layer made of a thermoplastic ultraviolet ray hardening resin formed on a substrate; a first stamping process of pressing, a single domain - 20 -

die on the surface of which a plurality of stamping irregularities are repeatedly formed along an optional direction, on said alignment film preliminary layer; a ultraviolet ray emitting process of disposing a mask formed with opening portions at suitable intervals, and emitting ultraviolet rays to said alignment . film preliminary layer through said mask; a second heating process of heating said operation film preliminary layer after said ultraviolet ray emitting Ξ. · <del>1,14,1</del> process; and a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of \_\_\_\_ irregularities are repeatedly formed along a direction different from said optional direction in said first stamping process, on said alignment . film preliminary layer. According to a preferred mode as described in claim 16, there is provided a method of manufacturing a stamping die for forming an alignment film for a liquid crystal element, comprising: a first heating process of heating a stamping film made of a thermoplastic ultraviolet ray hardening resin formed on a substrate; a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of - 21 -

irregularities are repeatedly formed along an optional direction, on said stamping film;

a ultraviolet ray emitting process of disposing a mask formed with opening portions at suitable intervals, and emitting ultraviolet rays to said stamping film through said mask;

a second heating process of heating said stamping film after said ultraviolet ray emitting process; and
a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along a direction different from said optional direction in said first stamping process, on said stamping film.

According to a preferred mode as described in claim 17, there is provided a method of manufacturing a stamping die for forming an alignment film for a liquid crystal element, comprising:

a first heating process of heating a stamping film made of a thermoplastic ultraviolet ray hardening resin formed on a substrate;

a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along an optional direction, on said stamping film;

a ultraviolet ray emitting process of disposing a mask formed with opening portions at suitable intervals, and emitting ultraviolet rays to said stamping film through said mask; a second heating process of heating said stamping film after said ultraviolet ray emitting process; and a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along a direction 7 different from said optional direction in said first stamping 3 process, on said stamping film; wherein the surface shape is formed on said stamping .5 die by electro-casting using said stamping film after said 108 stamping process as an original template. -2 According to a preferred mode as described in claim 18, Ž. there is provided a stamping apparatus used for pressing a die member having an irregular pattern on an alignment film preliminary layer on a substrate thereby stamping the irregular pattern on the upper surface of said alignment film preliminary layer, comprising: a press base body made of a rigid body; an elastic member disposed so as to face to said press base body; and a sheet-like die member provided on the side not facing - 23 -

to said press base body of said elastic member.

According to a preferred mode as described in claim 19, there is provided a stamping apparatus defined in the preferred mode as described in claim 18, wherein said elastic member is mounted on the surface of said press base body, and said die member is mounted on the surface of said elastic member.

According to a preferred mode as described in claim 20, there is provided a stamping apparatus for forming an irregular pattern on an alignment film defined in the preferred mode as described in claim 18 or 19, wherein said press base body is formed in a flat shape.

According to a preferred mode as described in claim 21, there is provided a stamping apparatus for forming an irregular pattern on an alignment film defined in the preferred mode as described in claim 18 or 19, wherein said press base body is formed in a roller shape.

According to a preferred mode as described in claim 22, there is provided a stamping apparatus defined in the preferred mode as described in any of claims 18 to 21, wherein said die member is formed to a thickness in the range of from 0.001 mm to 0.2 mm.

According to a preferred mode as described in claim 23, there is provided a stamping apparatus defined in the

preferred mode as described in any of claims 18 to 22, wherein a coating layer made of gold, gold alloy, copper or copper alloy is formed on the surface of said die member.

Hereinafter, the function of the present invention will be described.

According to the preferred mode as described in claim

1, since the surface shape of an alignment film is imparted
by pressing of a die, it is possible to eliminate the rubbing
process of generating dust, to accurately impart an optional
surface shape in accordance with the shape of the die to an
alignment film, and to impart uniform alignment domains
by an optional number; and further, since a plurality of
uniform alignment domains are formed in an effective
display plane, each visual field angle characteristic in
accordance with each uniform alignment domain can be
obtained, and a preferable visual field angle characteristic
in all the directions can be obtained as a whole.

. 王.

/A.

E

Since the surface shape of an alignment film is determined depending on the shape of the die, it is possible to easily form even the surface shape with irregularities of a magnitude of several  $\mu$ m $\times$   $\mu$ m, and hence to provide a high density liquid crystal element.

Since the surface of an alignment film is formed without a resist used in the conventional method, it is

- 25 -

possible to eliminate the problems such as disturbance of the surface shape of the alignment film and the damage of the underlayer alignemnt film which have been conventionally generated upon removal of the resist.

In the prior art structure of controlling a pretilt angle of liquid crystal by the surface shape of an alignment film formed by rubbing treatment, when the rubbing treatment is performed by a plural numbers using a resist as a mask for realizing a wide visual field angle, the surface shape of the alignment film at the boundary between the domain subjected to the first rubbing treatment and that subjected to the second rubbing treatment is disturbed, so that the width of the disturbed alignment of liquid crystal in the boundary is widened. On the contrary, according to the method of forming the surface shape of the alignment film by the die, the boundary in the aligned direction can be perfectly controlled, so that the width of the disturbed alignment is narrowed, thus improving the display quality.

Since the surface shape corresponding to the irregularities of a die can be imparted onto an alignment film, the number of uniform alignment domains to be formed for each pixel can be significantly increased as compared with the conventional manner. For example, for a pixel of  $100~\mu\text{m}\times100~\mu\text{m}$ , two pieces of domains can be formed in the

prior art; however, in the structure of the surface shape of the alignment film obtained by pressing of a die, since the irregularities formed on the surface of the die can be accurately stamped in the order of  $\mu$ m, several to several tens or more of alignment domains can be easily formed. Additionally, in this operation, the necessity of the positioning between the pixel and the alignment film is eliminated.

According to the preferred mode as described in claim 2, two directional uniform alignment domains in which aligned directions are substantially parallel to each other are formed on each pixel, and further the pretilt angle in another alignment film is low, so that when the substrates are superimposed, the positioning does not require the accuracy so much.

**3**27

\*

**13.** . .

**发** 

I

According to the preferred mode as described in claim 3 or 4, since the surface shape of an alignment film is formed by collection of the tilting surfaces of projecting portions, it is possible to specify the pretilt angle of liquid crystal by the tilting angle, and to specify the pretilt angle for each uniform alignment domain by the tilting surfaces of the projecting portions in each domain.

According to the preferred mode as described in claim 5, since the pretilt angle of liquid crystal molecules is

- 27 -

specified at 6° or more, the twisting angle of a liquid crystal molecules can be set at 240° or more. The twisting angle can be realized for an STN liquid crystal.

According to the preferred mode as described in claim 6, since the surface shape of an alignment film can be imparted by pressing of a die, an optional surface shape of an alignment film in accordance with the shape of the die can be accurately obtained, and the orientation film having uniform alignment domains by the desirable number can be obtained. Moreover, since a plurality of uniform alignment domains can be formed within an effective display plane, the visual field angle corresponding to each uniform alignment domain can be obtained, thus obtaining an excellent liquid crystal element having a preferable visual field angle in all the directions as a whole.

According to the preferred mode as described in claim 7, in addition to the first shape imparting process described in the preferred mode as described in claim 6, a second shape imparting process is provided of pressing a die capable of forming uniform alignment domains different in the emergent direction of the pretilt angle from those obtained in the first shape forming process, on the surface of the alignment film preliminary layer, so that different uniform alignment domains can be positively formed on a substrate,

- 28 -

and thereby a liquid crystal element excellent in a preferable visual field angle in all the directions as a whole can be obtained.

According to the preferred mode as described in claim 8, an alignment film with a surface shape having a low pretilt angle can be easily formed by pressing a roller having an elastic body on an alignment film, and thereby a liquid crystal element having upper and lower substrates being easy in the positioning can be provided.

2

2

3.

In the case of using a stamping die in which the tilting angle of tilting surfaces of projecting portions is 6° or more as described in the preferred mode as described in claim 9, the pretilt angle of liquid crystal becomes 6° or more, and accordingly, the liquid crystal having a twisting angle of 240° or more can be obtained. Thus, a liquid crystal element having a wide visual field angle can be obtained.

Moreover, in the case of using a stamping die in which a plurality of projecting portions having tilting surfaces described in the preferred mode as described in claim 10 are collected, a plurality of uniform alignment domains are easily formed on an alignment film, thus easily controlling the pretilt angle of liquid crystal.

According to the preferred mode as described in claim

- 29 -

11 or 12, there is provided a die used for forming an irregular surface shape on an alignment film preliminary layer on a substrate, wherein the tilting surfaces of the irregularities formed on the alignment film preliminary layer are specified for each of a plurality of domains, so that the alignment of liquid crystal is adjusted for each of the above domains. Accordingly, it is possible to manufacture an alignment film having a plurality of domains in each of which the alignment of liquid crystal is specified, and hence to obtain a liquid crystal element in which the alignment is specified for each domain.

Ĩ

The twisting angle of liquid crystal can be increased by specifying the tilting angle of the tilting surfaces of each projecting portion on the surface at 6° or more.

In the preferred mode as described in claim 13, since one projecting portion is taken as one uniform alignment domain, a plurality of domains each having a minimum size capable of being formed on the die can be formed on the alignment film, and the different alignment can be imparted to liquid crystal for each domain. As a result, it is possible to change the alignment of liquid crystal molecules in an extremely fine domain as compared with the conventional one, and hence to provide a liquid crystal element having a wide visual field angle.

In the method of manufacturing a transfer die for forming an orientation film for a liquid crystal element according to the preferred mode as described in claim 14, a stamping die used for formation of an alignment film subjected to alignment division can be manufactured at a low cost. As compared with the method of forming an alignment film by the rubbing treatment, the controllability is high, and it is possible to form a stable and high accurate alignment film having a high pretilt angle.

Differently from the method of forming an alignment film by the rubbing treatment, the shape imparting process is performed in a clean environment without generation of dust.

**2** 

In the method of forming an alignment film using the die, moreover, the manufacturing cost can be significantly reduced as compared with a method of preparing grating using photolithography.

In the method of forming an alignment film for a liquid crystal element according to the preferred mode as described in claim 15, an alignment film can be formed without manufacture of a stamping die having the surface shape aligned in a plurality of directions, and further as compared with the method of forming an alignment film by the rubbing treatment, the controllability is high, and it is

possible to form a stable and accurate alignment film having a high pretilt angle.

Differently from the method of forming an alignment film by the rubbing treatment, the shape imparting process is performed in a clean environment without generation of dust.

In addition, the manufacturing cost can be significantly reduced as compared with a method of preparing grating using photolithography.

In the method of manufacturing a stamping die for forming an alignment film for a liquid crystal element according to the preferred mode as described in claim 16, the stamping die can be manufactured without the stamping base die, thus reducing the manufacturing cost.

In the method of manufacturing a stamping die for forming an alignment film for a liquid crystal element according to the preferred mode as described in claim 17, the surface shape can be accurately stamped from a stamping base die to a stamping die using electro-casting.

Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which;

Fig. 1 is a sectional view showing the state in which an alignment film preliminary layer is formed on a substrate;

Fig. 2 is a side view showing the state in which a

plurality of projecting portions are formed on an alignment film preliminary layer using a stamping die; Fig. 3 is a partially enlarged perspective view showing irregularities of the stamping die; Fig. 4 is a partially enlarged view showing an irregular pattern formed on an alignment film preliminary layer using a stamping die; Fig. 5 is a partially enlarged perspective view for illustrating the shape of the irregular pattern shown in Fig. 4; Fig. 6 is a partial sectional view of the irregular pattern shown in Fig. 5; Fig. 7 is a partially enlarged sectional view showing another irregular pattern formed on an alignment film preliminary layer; Fig. 8 is a partially enlarged perspective view showing a further irregular pattern on an alignment film of the present invention; Fig. 9 is an equal contrast curve capable of realizing the twisting of 270° in STN liquid crystal; Fig. 10 is an equal contrast curve capable of realizing the twisting of 180° in STN liquid crystal; Figs. 11A to 11G are process diagrams showing a method of manufacturing a stamping die for forming an alignment - 33 -

film of a liquid crystal element;

Fig. 12 is a plan view showing one example of a mask used for manufacture of a stamping die for forming an alignment film for a liquid crystal element;

Fig. 13A is a process diagram of a prior art method showing an alignment film preliminary layer formed on a substrate;

Fig. 13B is a process diagram of the prior art method showing the state in which the alignment film preliminary layer is subjected to alignment treatment by rubbing;

Fig. 13C is a process diagram of the prior art method showing the state in which a resist is formed;

Fig. 13D is a process diagram of the prior art method showing the state in which part of the resist is removed;

Fig. 13E is a process diagram of the prior art method showing the state in which the second rubbing is performed on the resist part of which is removed;

Fig. 13F is a process diagram of the prior art method showing the alignment film obtained;

Fig. 13G is a sectional view showing an essential portion of a liquid crystal in which each domain is subjected to alignment division;

Fig. 14A is a process diagram of another prior art method showing an alignment film having a low pre-tilt

angle formed on a substrate; Fig. 14B is a process diagram of the another prior art method showing an alignment film having a high pre-tilt angle is formed on the alignment film having a low pre-tile angle; Fig. 14C is a process diagram of the another prior art method showing a resist formed on the alignment film having a high pre-tilt angle; Fig. 14D is a process diagram of the another prior art 2 method showing the state that part of the resist is removed  $\mathcal{Z}^{-}$ and further part of the alignment film having a high pre-7 -2. tilt angle is removed; Fig. 14E is a process diagram of the another prior art method showing the state in which rubbing is performed on the alignment film having a high pre-tilt angle part of which is removed; Fig. 14F is a sectional view showing an essential portion of a liquid crystal in which domain is subjected to alignment division; Fig. 15 is a view for illustrating a prior art structure in which alignment treatment is performed in two directions perpendicular to each other; Fig. 16 is a view showing a visual field angle characteristic of liquid crystal having the alignment film - 35 -

shown in Fig. 15;

Fig. 17 is a side view showing a first example of a stamping apparatus of the present invention;

Fig. 18 is a side view showing the state in which an irregular pattern is stamped on an alignment film preliminary layer formed on a substrate using the stamping apparatus shown in Fig. 17;

Fig. 19 is a side view showing a second example of a stamping apparatus of the present invention;

Fig. 20 is a side view showing the state in which an irregular pattern is stamped on an alignment film preliminary layer formed on a substrate using the stamping apparatus shown in Fig. 19;

Fig. 21 is a side view showing a third example of a stamping apparatus of the present invention;

Fig. 22 is a side view showing the state in which an irregular pattern in stamped. on an alignment film preliminary layer formed on a substrate using the stamping apparatus shown in Fig. 21;

Fig. 23 is a perspective view in which one example of the alignment film is enlarged;

Fig. 24A is a view showing the result of an interference light measurement test performed in Test Example;

Fig. 24B is a view showing the result of a separation test performed in Test Example;

Fig. 25A is a side view showing one example of a prior art stamping apparatus; and

Fig. 25B is a side view showing the state in which stamping is performed using the prior art stamping apparatus

Hereinafter, the present invention will be described in detail with reference to the drawings.

A liquid crystal element is manufactured in the following procedure: First, a resin solution is applied onto the upper surface of a substrate formed of glass or the like in a rectangular shape as shown in Fig. 1, by spincoating, screen printing or offset printing, and it is dried by baking, to thus form an alignment film preliminary layer 21.

7

II.

The alignment film preliminary layer 21 may be subjected to pre-baking and post-baking, as needed. The pre-baking and baking can be performed by a method wherein the substrate 20 formed with a resin solution is heated for about 30 minutes at 80°C and then heated for one hour at about 180°C. Alternatively, the substrate 20 is preliminarily heated at about 80°C, being coated with a resin solution by

screen printing, and is baked.

In the above-described screen printing, a resin solution is applied onto the substrate 21 in such a manner that a printing squeegee is moved by way of a screen provided on the substrate 20 in the longitudinal, transverse, or tilting direction of the substrate 21 at a specified speed, for example, 20 cm/sec.

The material of the substrate 20 is not limited to glass, and it may include those used for the liquid crystal element of this type, for example, ceramics. The shape of the substrate 20 is also not limited to the rectangular one, and it may include an optional one.

The alignment film preliminary layer 21 is preferably formed of a thermosetting resin being small in influence exerted on a stamping die (described later) such as epoxy resin, or a photo-curing resin. However, it may be formed of a thermoplastic resin. In this case, the thermoplastic resin preferably has a glass transition point in the range of from 130 to 280°C for ensuring the heat-stability of the liquid crystal element and also keeping the stability of the resin against heat treatment performed for stamping of an irregular pattern thereto by the stamping die (described later). The alignment film preliminary layer 21 made of the material satisfying such requirements is excellent in

- 38 -

heat resistance and it can be easily stamped with an irregular pattern (described later).

Next, a roller-like stamping die 23 shown in Fig. 2 is disposed on the upper surface of the alignment film preliminary layer 21 in the direction perpendicular to the longitudinal direction of the substrate 20. In such a state, at least one of the substrate 20 and the stamping die 23 is heated to a temperature near a glass transition temperature of the alignment film preliminary layer 21, and then the stamping die 23 is pressed on the alignment film preliminary layer 21 and simultaneously rolled in the longitudinal direction of the substrate 20.

The stamping die 23 is composed of a roller main body made of metal or the like, on the surface of which a resin film is formed. As shown in Fig. 3, on the surface of the resin film of the stamping die 23, an irregular pattern in which projecting portions 25 and recessed portions 26 are continuously formed in an alignment state. The irregular pattern includes irregularities along a first direction and irregularities along a second direction crossing the first direction, as shown in Fig. 3. In this irregular pattern, a pitch Pl of the irregularities along the first direction is specified to be shorter than a pitch P2 of the irregularities along the second direction.

The irregular pattern of the stamping die 23 can be thus stamped on the surface of the alignment film preliminary layer 21, to form an irregular pattern shown in Figs. 4, 5 and 6 on the upper surface of the alignment film preliminary layer 21. In the projecting portions 27 constituting the irregular pattern, as shown in Fig. 5, the pitch P1 of the irregularities along the first direction is specified to be shorter than the pitch P2 of the irregularities along the second direction, and a tilting angle  $\theta$  of a ridgeling of a tilting surface R2 extending along the second direction from the vertex portion of the projecting portion 27 is formed at, for example 20° or more.

In this irregular pattern having the structure shown in the figures, the pitch P1 is specified at, for example 3  $\mu$ m or less and the pitch P2 is, for example 50  $\mu$ m or less. The pitches P1 and P2, however, are not limited thereto, and for example, they may be specified at 1.2  $\mu$ m or less, and 20  $\mu$ m or less, respectively.

In this irregular pattern, moreover, as shown in Fig. 6, each projecting portion 27 of the irregularities along the second direction is formed in an approximately triangular shape being asymmetric in the right and left. Namely, the triangular shape of the projecting portion 27 is determined such that the angular ratio  $r_2/r_1$  is not equal to 1, wherein

 $r_2$  and  $r_1$  are respectively the right and left angles divided from the vertical angle of the triangle of the projecting portion 27 by a vertical line A extending from the vertex of the triangle. The projecting portion 27 may be formed into a shape similar to a sine wave, comb-shape or triangular shape, and of these shapes, the triangular shape is most suitable for improving the alignment of liquid crystal. In this triangular shape of the projecting portion 27, the vertex portion may be rounded or flattened. In the case where the projecting portion 27 is formed in a triangular shape, the above-described angular ratio  $r_2/r_1$  can be specified at 1.2 or more as shown in Fig. 6.

/g...

X

Incidentally, upon the above-described stamping operation, it is desirable that after the stamping die 23 is pressed on the alignment—film preliminary layer 21, the layer 21 is heated at a temperature near the glass transition temperature for a specified time, and the stamping die 23 is then rolled for stamping of the irregular pattern. The pressing force of the stamping die 23 applied at this time is suitably set in accordance with the hardness of the alignment—film preliminary layer 21, and is preferably set at, for example, about 50 kg/cm<sup>2</sup>. The moving speed of the stamping die 23 is preferably set at such a value as to perfectly stamping the irregular pattern, for example, at

- 41 -

about 15 mm/sec.

After the stamping die 23 is rolled to the center portion of the substrate 20, the substrate 20 and the stamping die 23 are cooled while the stamping die 23 is pressed on the substrate 20, and when they are cooled to a temperature not more than the glass transition temperature, the transfer die 23 is removed from the stamping film preliminary layer 21. The stamping die 23 is then turned by 180° and moved to the opposed end of the substrate 20, after which it is rolled from the end portion side in the same manner as described above for stamping of the irregular pattern. Alternately, after the stamping is completed at the center portion, the stamping die 23 is reversed by 180° over the substrate 20 for changing the direction of the irregular pattern, and it is rolled from the center portion for stamping of the irregular pattern in the same manner as described above. Thus, on the remaining portion of the substrate 20, a number of projecting portions 28 having tilting surfaces R3 different in the direction from tilting surfaces R2 of the projecting portions 27 of the irregular pattern previously formed, to thus form an alignment film The alignment film 29 has an uniform alignment 29. domain B1 composed of collection of a number of the projecting portions 27 having the tilting surfaces tilting at

- 42 -

the same tilting angle, and an uniform alignment domain B2 composed of the collection of a number of the projecting portions 28 having the tilting surfaces tilting at the tilting angle different from the above-described tilting angle of the tilting surfaces in the uniform alignment domain B1.

Two pieces of the substrates 20 with the alignment films 29 thus obtained are superimposed at a specified interval by way of a spacer or the like, and liquid crystal is sealed therebetween, to thus form a liquid crystal cell.

By forming a number of the projecting portions on the surface of the alignment film preliminary layer 21 as described above, the conventional rubbing treatment using a rubbing cloth is not required to be performed, to eliminate the process in which dust is generated, thus improving the manufacturing yield, and also the optional surface shape corresponding to that of the stamping die 23 can be imparted on the surface of the alignment film.

· \*\*\*

450 1780

-

۶ <del>د</del> مذ

Moreover, liquid crystal molecules corresponding to respective domains formed with the projecting portions 27, 28 being different in the direction of the tilting surface have respective pretilt angles different from in the direction, so that two uniform liquid crystal alignment domains can be formed in one pixel system. Accordingly, since the visual

field angle characteristic corresponding to respective domains can be obtained, the visual field angle characteristic being wider than conventional as a whole can be obtained.

In this example, the alignment film preliminary layer 21 is divided into two domains, and a number of the projecting portions 27 or 28 having the tilting surfaces tilting at the same direction are formed in each domain. layer 21 on the substrate 20 may be divided into a plurality of domains, and a number of projecting portions having a specified tilting direction can be formed on each of a plurality of the divided domains. In this case, a plurality of domains are set on the surface of the stamping die 23, and projecting portions having tilting surfaces tilting in the same direction are formed on each of a plurality of domains. Such a stamping die is rolled on the alignment film preliminary layer 21 once, so that a number of domains each including a plurality of projecting portions having tilting surfaces tilting in the same direction can be formed on the surface of the alignment film preliminary layer 21. In addition, since the pretilt angles (described later) of liquid crystal is specified on the base of the tilting surfaces R2 and R3 of the projecting portions 27 and 28, there can be obtained an alignment film having a plurality

- 44 -

of domains each having alignment corresponding to the tilting directions of the tilting surfaces R2 and R3 of the projecting portions 27 and 28.

For example, as shown in Fig. 7, three pieces of the projecting portions 27 having the tilting surfaces R2 tilting at an angle are continuously formed on a domain, and on each side of the domain, three pieces of the projecting portions 28 having the tilting surfaces R3 tilting at another angle are continuously formed, to form an alignment film 29' on the surface of which a number of irregular patterns are orderly arranged. A stamping die 30 used in this case has an irregular shape shown in Fig. 7 in which recessed portions 27' corresponding to the projecting portions 27 and recessed portions 28' corresponding to the projecting portions 28 are formed.

---

-

By pressing such a stamping die 30 on the alignment film preliminary layer 21 once, a number of uniform alignment domains each having tilting surface tilting at the same angle can be easily formed on the alignment film preliminary layer 21.

Fig. 8 shows another example of a stamping die for forming an alignment film. In the stamping die 31, a number of projecting portions 32 each having a cross-sectional shape similar to a sine wave are formed in an

- 45 -

alignment state. In this example, the tilting angle of the ridgeling of a tilting surface extending along the second direction from the vertex portion of the projecting portion 32 is formed to be more than that in the stamping die in the previous example. Using the stamping die 31 having the projecting portions 32 of such a high tilting angle, an alignment film having a large pretilt angle can be easily formed.

In particular, the setting of the tilting angle of the tilting surface of the projecting portion at a value higher than 20° or more, is effective for the STN liquid crystal.

In general, the twisting angle of the STN liquid crystal is in the range of from 180 to 240°; however, by increasing the twisting angle more than the above-described range, the visual field angle can be increased. To set the twisting angle of the STN liquid crystal at 240° or more, the pretilt angle of the liquid crystal molecules are required to be set at 15° or more. In an alignment film subjected to rubbing treatment using a rubbing cloth, however, the pretilt angle of 15° or more cannot be realized.

On the other hand, according to the method of using the stamping die having the above-described structure, the projecting portions 27, 28 having the tilting angle of 20° or more can be easily formed on a large scale, and accordingly,

the pretilt angle of liquid crystal molecules can be easily controlled at a value of 20° or more. Thus, in the STN liquid crystal, the twisting angle of 270° can be realized, and thereby a liquid crystal element of a wide visual field angle can be produced on a large scale.

Fig. 9 is an equal contrast curve of an STN liquid crystal having a twisting angle of 270°, which shows the dependency of an visual field angle on a visual field angle. The numerals around the concentric circles (0°, 90°, 180°, and 270°) show the directions along which the liquid crystal element is viewed. The concentric circle indicates the tilting degree from the normal line of the surface of the display element for each 10°, and the outermost circle indicates the state tilting from the normal line by 60°.

3

Æ

7

Fig. 10 is an equal contrast curve of an STN liquid crystal having a twisting angle of 180°, in which the slant line portion shows the reversed domain. From this figure, it is revealed that the twisting angle of 270° in the STN liquid crystal can be realized and a high contrast domain can be widely obtained.

The alignment film having a plurality of domains each having the same alignment is manufactured in the following procedure.

First, a thermoplastic ultraviolet ray hardening resin

- 47 -

is flatly applied onto on a substrate of a stamping base die, to form a stamping film.

As the thermoplastic ultraviolet ray hardening resin, there may be used polyvinyl cinnamate or polyvinyl benzalacetophenone.

Next, in a first heating process, the stamping base die is heated, to soften the stamping film.

On the other hand, a single domain stamping die 18 on which a plurality of irregularities are repeatedly formed along an optional direction is separately prepared. Then, as shown in Fig. 11A, the single domain stamping die 18 is pressed on the soften stamping film 15, to thus stamping the irregularities of the single domain stamping die 18 on the stamping film 15 (first transfer process).

As shown in Fig. 11B, a mask formed with opening portions 24 spaced at suitable intervals is disposed on the stamping film 15, and ultraviolet rays having a wavelength of from 220 to 400 nm are emitted over the mask 19 (ultraviolet ray emission process), to harden only portions of the stamping film 15 corresponding to the opening portions of the mask 19.

The mask 19 has preferably a stripe pattern in which opening portions 22 and shielding portions 24 are periodically repeated at specified intervals. The width of

the opening portion 22 is determined in accordance with the size of the domain to be formed, and it is preferably 50  $\mu m$  or more.

In addition, the opening portion of the mask 19 is sufficient to allow ultraviolet rays to transmit therethrough.

As shown in Fig. 11C, the stamping film 15 is heated (second heating process). At this time, only a portion, not emitted with ultraviolet rays in the previous process, of the stamping film 15 formed on the substrate 14 of the stamping base die 34 is softened.

\*

After that, a single domain stamping die 33 in which a plurality of irregularities repeatedly formed along the direction different from that in the single domain stamping die 18 used in the first stamping process is pressed on the stamping film 15, to stamp the irregularities of the single domain stamping die 33 on the stamping film 15 (second stamping process).

The single domain stamping die 33 used in the second stamping process may be different from, or the same as the single domain stamping die 18. In the case where the single domain stamping die 18 is used as the single domain stamping die 33, it is changed in the direction relative to the stamping base die 34, for example, the stamping base die 34

or the single domain stamping die 18 is changed by 90 or 180° and is pressed on the stamping film 15.

By adjustment of the domain on which ultraviolet rays emitted or the number of stamping by means of the single domain stamping die, an alignment film formed with irregularities having three or more kinds of directions or tilting angles, can be manufactured.

The whole stamping film 15 is then hardened by emission of ultraviolet rays on the whole stamping film 15, to thus form the stamping base die 34 in which the stamping film 15 having irregularities extending in the two directions are formed on the substrate 14, as shown in Fig. 11E.

Next, as shown in Fig. 11F, a flat stamping die 35 is pressed on the stamping film 15 of the stamping base die 34, to be stamped with the surface shape of the stamping film 15, thus manufacturing the stamping die 35 for forming an alignment film of a liquid crystal element as shown in Fig. 11G.

An alignment film having irregularities extending along a plurality of directions can be also formed without the above-described stamping base die.

Namely, in the method of manufacturing the stamping die for forming an alignment film of a liquid crystal element,

the substrate 14 of the stamping base die 34 is taken as an alignment film substrate and the stamping film is taken as an alignment film. Referring again to Figs. 11A to 11G, this manufacturing method will be described below.

First, a thermoplastic ultraviolet ray hardening resin is flatly applied onto a substrate which is the underlayer of an alignment film, to form an alignment film preliminary layer. Next, as a first heating process, the alignment film preliminary layer is heated to be soften.

On the other hand, a single domain stamping die 18 on which a plurality of irregularities are repeatedly formed along an optional direction is separately prepared. Then, as shown in Fig. 11A, the single domain stamping die 18 is pressed on the soften alignment—film preliminary layer 15, to thus stamping the irregularities of the single domain stamping die 18 on the alignment—film preliminary layer 15 (first stamping process).

As shown in Fig. 11B, a mask formed with opening portions 24 spaced at suitable intervals is disposed on the alignment film preliminary layer 15, and ultraviolet rays are emitted over the mask 19 (ultraviolet ray emission process), to harden only portions of the alignment film preliminary layer 15 corresponding to the opening portions of the mask 19. In addition, the opening portion of the mask 19

is sufficient to allow ultraviolet rays to transmit therethrough.

As shown in Fig. 11C, the alignment film preliminary layer 15 is heated (second heating process). At this time, only a portion, not emitted with ultraviolet rays in the previous process, of the alignment film preliminary layer 15 is softened.

After that, a single domain stamping die 33 on which a plurality of irregularities repeatedly formed along the direction different from that in the single domain stamping die 18 used in the first stamping process is pressed on the alignment film preliminary layer 15, to stamping the irregularities of the single domain stamping die 33 on the alignment film preliminary layer 15 (second stamping process).

The single domain stamping die 33 used in the second stamping process may be different from, or the same as the single domain stamping die 18. In the case where the single domain stamping die 18 is used as the single domain stamping die 33, it is changed in the direction relative to the stamping base die 34, for example, the stamping base die 34 or the single domain die 18 is changed by 90 or 180° and is pressed for stamping.

By adjustment of the domain on which ultraviolet rays

emitted or the number of stamping by means of the single domain stamping die, an alignment film preliminary layer formed with irregularities having three or more kinds of directions or tilting angles, can be manufactured.

The whole alignment film preliminary layer 15 is then hardened by emission of ultraviolet rays on the whole alignment film preliminary layer 15, to thus form the alignment film having irregularities extending in the two directions are formed on the substrate 14, as shown in Fig. 11E.

 $\equiv$ 

----

\_\_\_\_

Moreover, in the stamping apparatus for stamping an irregular pattern according to the present invention, a thin die member is mounted on a press base body by way of an elastic member. With this stamping apparatus in the case where an irregular pattern is stamped by pressing the die member on an alignment film preliminary layer, even when the alignment film preliminary layer is tilted somewhat relative to the press base body, the elastic member ca be deformed in accordance with the tilting of the alignment film preliminary layer, with a result that the irregular pattern of the die member can be positively pressed on the whole surface of the alignment film preliminary layer.

In the case of using the die member having a thickness

of from 0.001 to 0.2 mm, even when the alignment film preliminary layer has slight waviness, irregularities or tilting due to the fine waviness, irregularities or tilting of the substrate, the elastic member and die member are positively deformed in accordance with the waviness, irregularities or tilting, and thereby the irregular pattern of the die member can be positively pressed on the whole surface of the alignment film preliminary layer. Namely, by the use of the die member having a thickness of 0.2 mm or less, the elastic member and the die member can sufficiently follow the waviness, irregularities or tilting of the substrate or alignment film preliminary layer. In addition, if the elastic member has a thickness of 0.001 mm or more, it never causes any problem such as breakage in handling.

By provision of a coating layer made of gold or copper on the surface of the die member, the alignment film preliminary layer can be prevented from being stuck on the die member when an irregular pattern is stamped on the alignment film preliminary layer and then the die member is removed from the alignment film preliminary layer.

The press base body may be formed in a flat plate or roller-like shape. In the case of the flat plate-like press base body mounted with an elastic member and an die member,

operation. On the other hand, in the case of roller-like base body, an irregular pattern can be stamped by pressing the base body while rolling it along an alignment film preliminary layer on the substrate.

The present invention will be more clearly understood by way of the following examples. However, it is noted that the present invention is not limited thereto.

## Example 1

In this example, the present invention is applied to a twisted nematic liquid crystal element.

A rectangular glass substrate for a liquid crystal element, on the surface of which an electrode was formed, was prepared. On the surface of the substrate, a solution of  $\gamma$ -butyllactam containing 5 wt% of polyether sulfan (trademark name: PES, produced by Mitsui Toatsu) was printed to a thickness of 0.1  $\mu$ m by screen printing, to form a solution layer. At this time, to form the solution layer, a printing squeegee was moved along the longitudinal direction of the glass substrate at a speed of about 20 cm/sec.

The substrate formed with the solution layer was prebaked for 30 seconds at 30°C, and further baked for one hour at 180°C, to dry the solution layer, thus forming an alignment film preliminary layer. Alternatively, the

- 55 -

solution may be printed on the glass substrate which has been preliminarily heated at 80°C.

A columnar stamping die made of epoxy resin, on the surface of which an irregular pattern was formed as shown in Fig. 3, was set on the alignment film preliminary layer. In such a state, the alignment film preliminary layer was heated at 240°C and held for 5 minutes at 240°C, and then the stamping die was pressed on the alignment film preliminary layer at a pressure of 50 kg/cm² and simultaneously rolled at a moving speed of 15 mm/min, to stamping the irregular pattern of the stamping die on the alignment film preliminary layer.

An irregular pattern shown in Fig. 4 was thus stamped on the surface of the alignment film. In the irregular pattern, projecting and recessed portions each having an approximately triangular shape were repeatedly formed along the moving direction of the printing squeegee, that is, along the longitudinal direction of the glass substrate. The height of the projecting portion was 0.2  $\mu$ m; the length of the tilting surface was 2  $\mu$ m; and the interval between the projecting portions arranged in the right and left was 0.3  $\mu$ m. In this example, the uniform alignment domain had a size of 30×30  $\mu$ m.

Two pieces of the substrates, each being formed with

such an alignment film, were superimposed in such a manner as to be separated from each other at a specified interval by way of a spacer, and TN liquid crystal (trademark name: K-15, produced by CHISSO CORPORATION) was sealed therebetween, to prepare a liquid crystal cell.

The visual field angle of the liquid crystal element thus obtained was about 40° in the transverse direction, and about 40° in the vertical direction.

On the contrary, the visual field angle of the liquid crystal element having the same structure except that the uniform alignment domain was not provided, was about 30° in the transverse direction, about 10° in the upward direction, and about 20° in the downward direction.

In the previous process, the moving direction of the printing squeegee is desirable to be substantially the same as the arrangement direction of nearly triangular projecting portions; however, the moving direction of the printing squeegee is not necessarily taken as the longitudinal direction of the substrate, but it may be taken as the transverse or tilting direction.

## Example 2

The solution used in Example 1 was replaced with a solution containing 2 wt% polyvinyl alcohol (trademark name: NM-14, produced by The Nippon Synthetic Chemical Industry

Co., Ltd.) using pure water as a solvent. The solution was applied on a substrate by spin-coating. Subsequently, the substrate formed with the solution layer was preliminarily heated for one minute at 50°C and further heated for one hour at 120°C, to dry the solution, thus preparing an alignment film preliminary layer having a thickness similar to that in Example 1.

The substrate and a roller type stamping die shown in Fig. 2 were heated at 180°C and 100°C, respectively, and the stamping die was pressed on the alignment film preliminary layer, and simultaneously rolled, to stamp an irregular pattern formed on the surface of the stamping die onto the alignment film preliminary layer, thus manufacturing an alignment film. Two pieces of the substrates thus obtained were superimposed in the same manner as in Example 1, to manufacture a liquid crystal cell having a visual field angle similar to that in Example 1.

## Example 3

A solution of 1,1,1,3,3,3-hexafluoro-2-propanol containing 5% of high molecular liquid crystal (produced by Asahi Denka Kogyo) was applied onto a rectangular glass substrate similar to that used in Example 1, to form an alignment film preliminary layer. The alignment film preliminary layer alignment film

80°C, and further dried for one hour at 180°C.

on the alignment film preliminary layer and simultaneously rolled along the longitudinal direction of the substrate, to stamp an irregular pattern of the stamping die onto the alignment film preliminary layer. The stamping die was formed by a method wherein a fluoro-rubber (trademark name: Bytone, produced by SUMITOMO 3M LIMITED) having a thickness of 3 mm was wound by hand around the surface of a stainless steel made cylindrical core material having a diameter of 300 mm. The width of the roller portion of the stamping die was formed to be wider than the width of the substrate. The peripheral speed of the stamping die was 1 mm/sec, and the pressing force of the stamping die onto the substrate was 5 kg/cm<sup>2</sup>.

<u>~</u>

In the glass substrate having the alignment film thus formed, a refractive factor nA relative to polarization in the longitudinal direction was different from a refractive factor nB relative to polarization in the transverse direction. The refractive factor nA was maximized in the plane and the refractive factor nB perpendicular to the refractive factor nA was minimized. A difference therebetween  $\Delta n$  was  $2.86 \times 10^{-2}$ .

The anisotropy of the refractive factor means that the

- 59 -

main chains of the molecules forming the alignment film formed on the surface of the glass substrate directs in the longitudinal direction of the glass substrate.

## Example 4

A stamping die, used for forming an alignment film having a plurality of domains each of which has a specified alignment, was manufactured.

First, polyvinyl cinnamate as a thermoplastic ultraviolet ray hardening resin was flatly applied onto a substrate of a stamping base die, to form a stamping film. The stamping base die was heated at 130°C, to soften the stamping film. The thickness of the stamping film was 200 nm (100 nm, even at the thinnest portion).

A single domain stamping die, in which a plurality of irregularities were repeatedly formed on the surface along an optional direction, was pressed on the softened stamping film for 5 minutes at a pressure of 100 kg/cm², to stamp the irregularities of the single domain stamping die on the stamping film.

Next, a mask shown in Fig. 12 in which the pitch of opening portions was specified at 50  $\mu m$  for dividing one pixel into two parts was set on the stamping film, and ultraviolet rays of 100 mW/cm² was emitted onto the stamping film through the mask for 5 minutes using an ultraviolet ray

lamp having a power of 4.5 kW and a wavelength of 375 nm, to harden only a portion, corresponding to the opening portions of the mask, of the stamping film.

The mask was formed of a substrate made of quartz glass having a thickness of 3 mm on which shielding portions made of a Cr film having a thickness of 140 nm were formed.

The stamping film was heated again to soften a portion of the stamping film not emitted with ultraviolet rays, and the above-described single domain stamping die was rotated by 180° and pressed on the stamping film. Ultraviolet rays were then emitted over the stamping film to harden the whole stamping film. Subsequently, the stamping base die was pressed on a flat stamping die, to stamp the surface shape of the stamping base die onto the flat stamping die, thus manufacturing the stamping die for forming an alignment film for a liquid crystal element.

4

Differently from the above-described method of manufacturing a stamping die for forming an alignment film from the stamping base die prepared using a single domain stamping die, a stamping die for forming an alignment film can be directly manufactured from a single domain stamping die without a stamping base die.

#### Example 5

An alignment film having a plurality of domains each

- 61 -

of which has a specified alignment was manufactured.

First, polyvinyl cinnamate as a thermoplastic ultraviolet ray hardening resin was flatly applied onto a substrate, to form an alignment film preliminary film. The alignment film preliminary layer was heated at 130°C, to soften the alignment film preliminary film. The thickness of the stamping film was 200 nm (100 nm, even at the thinnest portion).

A single domain stamping die, in which a plurality of irregularities were repeatedly formed on the surface along an optional direction, was pressed on the softened alignment film preliminary layer for 5 minutes at a pressure of 100 kg/cm<sup>2</sup>, to stamp the irregularities of the single domain stamping die on the alignment film preliminary layer.

A mask shown in Fig. 12 in which the pitch of opening portions was specified at 50  $\mu$ m for dividing one pixel into two parts was set on the alignment film preliminary layer, and ultraviolet rays of 100 mW/cm² was emitted onto the alignment film preliminary layer through the mask for 5 minutes using an ultraviolet ray lamp having a power of 4.5 kW and a wavelength of 375 nm, to harden only a portion, corresponding to the opening portions of the mask, of the alignment film preliminary layer.

The mask was formed of a substrate made of quartz glass

having a thickness of 3 mm on which shielding portions made of a Cr film having a thickness of 140 nm were formed.

The alignment film preliminary layer was heated again to soften a portion of the alignment film preliminary layer not emitted with ultraviolet rays, and the above-described single domain stamping die was rotated by 180° and pressed on the alignment film preliminary layer. After that, ultraviolet rays were emitted over the alignment film preliminary layer to harden the whole alignment film preliminary layer, thus forming the alignment film for a liquid crystal element.

#### Example 6

Fig. 17 shows an example of a stamping apparatus of the present invention. A stamping apparatus 110 includes a press substrate 111, a sheet-like elastic member 112 mounted on the lower surface of the press substrate 111, and a sheet-like die member 113 mounted on the lower surface of the elastic member 112.

The press substrate 111 is made of a metal material having a high rigidity, and the lower surface thereof is accurately ground by a grinding means. The surface roughness of the press substrate 111 is preferably adjusted at, for example, about  $\pm 10~\mu m$ .

The elastic member 112 is formed of a resin layer

having a thickness of from 0.8 to several mm. The resin layer is preferably made of silicon rubber.

The die member 113 is made of nickel, gold or copper, and has a thickness preferably in the range of from 0.01 to 0.2 mm. In the die member 113, an irregular pattern is formed on the surface of the flat base body. The portion of the irregular pattern on the surface of the die member 113 is covered with a film layer made of gold, gold alloy, copper or copper alloy. The film layer is formed on the irregular pattern to a thickness of from 0.1 to 0.5  $\mu$ m by vapor deposition or sputtering.

In Fig. 17, reference numeral 115 indicates a transparent substrate made of glass; and 116 is an alignment film preliminary layer made of aromatic polyamide covering the substrate 115. In the drawing, the waviness of the substrate 115 is emphasized; however, the camber and the irregularities of the substrate 115 are specified to be in the order of  $\mu m$  or less.

The irregular pattern is stamped on the alignment film preliminary layer 116 in the following procedure. The die member 113 of the stamping apparatus 110 is set on the alignment film preliminary layer 116 and is pressed thereon as shown in Fig. 18.

In this case, even when the waviness or irregularities

are generated somewhat on the substrate 115, they can be absorbed by the deformation of the die member 113 and the elastic member 112 as shown in Fig. 18. This is because the die member 113 is thin and excellent in flexibility, and the elastic member 112 can be elastically deformed. As a consequence, the die member 113 can be positively pressed on the alignment film preliminary layer 116. At this time, the pressing temperature is preferably in the range of from 100 to 200°C and the pressing force is preferably in the range of from 50 to 100 kg/cm<sup>2</sup>.

The irregular pattern corresponding to that of the die member 113 is stamped on the alignment film preliminary layer 116. The alignment film preliminary layer 116 is thus taken as an alignment film.

After the stamping of the irregular pattern, the die member 113 is separated from the alignment film. At this time, since the covering layer made of gold, gold alloy, copper or copper alloy is present on the surface of the die member 113, part of the alignment film is difficult to be stuck on the die member 113, and to be peeled to the die member 113 side. The irregular pattern can be thus positively stamped. Namely, the alignment film preliminary layer 116 is difficult to be stuck on the covering layer made of gold or copper formed on the surface

of the die member 113 due to a difference in the surface energy between aromatic polyamide constituting the alignment film preliminary layer 116 and gold or copper. Thus, it is possible to manufacture an alignment film stamped with the irregular pattern without harming part of the alignment film preliminary layer.

As described above, gold or copper is difficult to be stuck on the alignment film preliminary layer 116 on the basis of a difference in the surface energy between the alignment film preliminary layer and gold or copper, and the same effect can be obtained when gold or copper is replaced with a gold alloy or copper alloy added with another element such as nickel.

#### Example 7

Figs. 19 and 20 show another stamping apparatus of the present invention. A transfer apparatus 120 includes a roller (press base body) 121, a flat elastic body 122 provided separately from the roller 121, and a die member 123 integrated with the lower surface of the elastic member 122. The elastic member 122 has the same structure as that of the elastic member 112 of the previous example, and the die member 123 has the same structure as that of the die member 123 in the previous example.

In this example, as shown in Fig. 19, the die member

113 is placed on an alignment film preliminary layer 116 of the substrate 115, and in such a state, the roller 121 is pressed on the elastic member 122 and is simultaneously rolled from one side of the substrate 115 to the other side. With this operation, the irregular pattern of the die member 123 is stamped on the alignment film preliminary layer 116 while the elastic member 122 and the die member 123 are respectively deformed in accordance with the waviness and the irregularities of the substrate 115.

In the case using the transfer apparatus 120, the same effect as in Example 6 can be obtained.

#### Example 8

\*\*\*\*

Figs. 21 and 22 show a further stamping apparatus of the present invention. A stamping apparatus 130 includes a roller (press base body) 131, a sheet-like elastic member 122 stuck on the surface of the roller 131, and a die member 133 stuck on the surface of the elastic member 132. The elastic member 132 has the same structure as that of the elastic member 112 in the previous example, and the die member 133 has the same structure as that of the die member 131 in the previous example.

In this apparatus, as shown in Fig. 22, the roller 131 is placed on an alignment film preliminary layer 116 of the substrate 115, and in such a state, the elastic member 132 on

the surface of the roller is pressed on the alignment film preliminary layer 116 at a specified pressure, and is simultaneously rolled from one side of the substrate 115 to the other side. With this operation, the irregular pattern of the die member 133 is stamped onto the alignment film preliminary layer 116 while the elastic member 132 and the die member 133 are respectively deformed in accordance with the camber and irregularities of the substrate 115.

In the case of using the stamping apparatus 130, the same effect as in Example 6 can be obtained.

Fig. 23 shows one example of an alignment film having the irregular pattern formed using each of the stamping apparatuses in Examples 6, 7 and 8. The alignment film 140 has an irregular pattern desirable to specify a pretilt angle of liquid crystal.

The irregular pattern in this example is formed of the collection of a number of triangular projecting portions 141 along the first and second directions shown by the arrows in the figure. A pitch P1 of the irregularities along the first direction is set to be shorter than a pitch P2 of the irregularities along the second direction. For example, the pitch  $P_1$  is 3.0  $\mu$ m or less, and the pitch  $P_2$  is 50  $\mu$ m or less. The height (depth)  $d_1$  of the projecting portion 141 is, for example 0.5  $\mu$ m or less.

#### Test Example 1

A stamping apparatus used in this test example has a structure shown in Fig. 17, that is, it is integrally provided with a flat substrate made of tool steel (specified by JIS SK4), a sheet-like elastic member made of silicon rubber having a thickness of 0.8 mm, and a die member made of nickel. An irregular pattern stamping test was carried out using this stamping apparatus. An irregular pattern was stamped on an alignment film preliminary layer made of aromatic polyamide having a thickness of 0.2  $\mu$ m formed on a glass substrate having a thickness of 1.1 mm. The stamping pressure was 100 kg/cm². The irregular pattern was as shown in Fig. 23, wherein the pitch in the first direction was 0.3  $\mu$ m, the pitch in the second direction was 2  $\mu$ m, and the height of the projecting portion was 0.2  $\mu$ m.

Eight kinds of stamping apparatuses were experimentally manufactured using eight kinds of die members having thicknesses of 3 mm, 1mm, 0.5 mm, 0.2 mm, 0.05 mm, 0.015 mm, 0.005 mm and 0.001 mm. Using each of these stamping apparatuses, an irregular pattern stamping test was carried out. A gold evaporation film having a thickness of 0.1  $\mu$ m was formed on the surface having the irregular pattern. In addition, a die member having a thickness of 0.001 mm or less was intended to be manufactured; however, it could not be

manufactured because of being poor in strength.

The alignment film thus obtained was subjected to an interference light measurement test, and to stamp ratio measurement test. The results are shown in Table 1. In the interference light measurement test, the presence or absence of the interference light generated when light is emitted onto the alignment film is visually observed. The results are shown in terms of the area. One example is typically shown in Fig. 24A. In Fig. 24A, the interference light is recognized in a domain A where stamping is performed; and the interference light is not recognized in a domain B where stamping is not performed.

In the transfer ratio measurement test, the ratio of the depth of a groove of the recessed portion in the irregular pattern of a die member to the depth of a groove of the irregular pattern of the alignment pattern is measured as the stamping ratio.

The depth of the groove is measured by a method wherein the average value in a plane as the depth of the groove is measured by AFM (Atomic Force Microscope).

Table 1

thickness of die	domain of interference	stamping ratio (%)
member (mm)	light (%)	
3	< 30	< 30
1	< 50	<b>&lt;</b> 50
0.5	< 50	<b>&lt;</b> 50
0.2	< 100	< 90
0.05	< 100	< 90
0.03	< 100	90
0.015	< 100	< 95
0.005	< 100	< 95
0.001	< 100	< 95

As is apparent from Table 1, in the case of using a die member having a thickness of 0.2 mm, the interference light generating domain is nearly 100%, that is, the stamping is perfectly performed; and in this case, the stamping ratio is as high as about 90%. Moreover, in the case of using a die member having a thickness of 0.015 mm or less, the stamping ratio is 95%.

#### Test Example 2

Next, three kinds of stamping dies, in each of which a die member had a thickness of 0.05 mm and the covering layer

formed on the surface of the die member was made of either of gold, copper or nickel, were experimentally manufactured. The stamping of an irregular pattern was performed using each of the die members. It was observed whether or not a separated alignment film preliminary layer was stuck on the surface of the die member.

As a result, in the case of the nickel covering layer, as shown in Fig. 24B, a separation portion having a diameter of from 0.5 to 3 mm was stuck in a dotted manner. It was revealed that the sticking domain with the alignment film was 30% or less. In addition, in the stamping apparatus using a die member formed with a gold covering layer or a copper covering layer, there was not recognized a phenomenon in which the alignment film preliminary layer was stuck on the die member.

CLAIMS A liquid crystal element comprising: a pair of substrates disposed so as to face to each other, and having respective alignment films on the facing surfaces thereof; and liquid crystal held between said substrates; wherein a surface shape of said alignment film formed on at least one of said substrates is formed by pressing of a die, and said alignment film formed with the surface shape by pressing of the die has a plurality of uniform alignment domains which are different from each other in the emergent direction or emergent magnitude of a pretilt angle of liquid crystal within an effective display plane. A liquid crystal element according to claim 1, wherein said alignment film formed on one of said substrates and having a plurality of said uniform alignment domains has two directional uniform alignment domains in which the emergent directions of the pretilt angle of liquid crystal are approximately parallel to each other, and said alignment film formed on the other of said substrates has a pretilt angle lower than said pretilt angle in one of said substrates. - 73 -

- 3. A liquid crystal element according to claim 1 or 2, wherein the surface shape of said alignment film is formed by collection of a plurality of projecting portions having tilting surfaces, and said tilting surfaces of said projecting portions function as a means of adjusting the pretilt angle of liquid crystal.
- 4. A liquid crystal element according to any of claims 1 to 3, one uniform alignment domain having an emergent direction or emergent magnitude of a pretilt angle of liquid crystal is formed by the collection of first projecting portions having tilting surfaces extending at a tilting angle, and the other uniform alignment domain having an emergent direction or emergent magnitude of a pretilt angle different from that in said one uniform alignment domain is formed by collection of a plurality of second projecting portions having tilting surfaces extending at an angle different from that of said tilting surfaces of said first projecting portions.
- 5. A liquid crystal element according to any of claims 1 to 4, wherein the surface shape of an alignment film is formed by collection of projecting portions having tilting surfaces, and the tilting angle of the tilting surfaces of said projecting portions formed on the surface of said alignment film is specified at 6° or more.

- 74 -

A method of manufacturing a liquid crystal element having liquid crystal held between a pair of substrates, said substrates being disposed so as to face to each other and having respective alignment films on the facing surfaces thereof; comprising: an alignment film preliminary layer forming process of forming an alignment film preliminary layer on the surface of each of said substrates; and a shape imparting process of pressing a die capable of forming a plurality of uniform alignment domains different from each other in an emergent direction or emergent magnitude of a pretilt angle of liquid crystal within an effective display plane on the surface of said substrate, on the surface of at least one of said alignment film preliminary layer. A method of manufacturing a liquid crystal element 7. having liquid crystal held between a pair of substrates, said substrates being disposed so as to face to each other and having respective alignment films on the facing surfaces

thereof; comprising:

alignment film preliminary layer forming process of forming an alignment film preliminary layer on the surface of each of said substrates; and

a first shape imparting process of pressing a die

capable of forming uniform alignment domains nearly equal to each other in an emergent direction or emergent magnitude of a pretilt angle of liquid crystal within an effective display plane on the surface of said substrate, on the surface of at least one of said alignment film preliminary layer; and

a second shape imparting process of pressing a die capable of forming uniform alignment domains different in the emergent direction of the pretilt angle from those obtained in said first shape forming process, on the surface of said alignment film preliminary layer.

- 8. A method of manufacturing a liquid crystal element according to claim 6 or 7, which further comprises a shape imparting process of pressing said die on one of said alignment film preliminary layers, and a process of pressing an approximately cylindrical roller formed at least on the surface with an elastic body on the other of said alignment film preliminary layers.
- 9. A method of manufacturing a liquid crystal element according to any of claims 6 to 8, wherein said uniform alignment domains are formed using a stamping die in which a plurality of projecting portions having tilting surfaces are formed on the surface and the tilting angle of said tilting surfaces of said projecting portions is specified at

- 76 -

direction, wherein the tilting direction of said tilting surfaces formed by said irregularities are specified for each of a plurality of divided domains formed on the surface of said stamping die. A stamping die for forming an alignment film for a 12. liquid crystal element according to claim 11, wherein the tilting angle of said tilting surfaces of said projecting portions formed on the surface of said stamping die is specified at 6° or more. A stamping die for forming an alignment film for a 13. liquid crystal element according to claim 11 or 12, wherein said divided domain of said stamping die is equivalent to one of said projecting portions formed on said stamping die. A method of manufacturing a stamping die for forming an 14. film for a liquid crystal element comprising: alignment a first heating process of heating a stamping film made of a thermoplastic ultraviolet ray hardening resin formed on a substrate; a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along an optional direction, on said stamping film; a ultraviolet ray emitting process of disposing a mask - 78 -

6° or more.

- 10. A method of manufacturing a liquid crystal element according to any of claims 6 to 9, wherein said shape imparting process is carried out using a die on the surface of which a plurality of first portions each forming one uniform alignment domain and a plurality of second portions each forming the other uniform alignment domain are formed, said first portion being constituted of collection of a plurality of projecting portions with tilting surfaces having the same tilting direction and the same tilting angle, and said second portion being constituted of a plurality of projecting portions with tilting surfaces having a tilting direction and a tilting angle different from said tilting direction and said tilting angle of said first portion.
- 11. A stamping die for forming an alignment film for a liquid crystal element, which is pressed on the surface of a resin made alignment film preliminary layer formed on a substrate for a liquid crystal element for forming a plurality of projecting portions on the surface of said alignment film preliminary layer, comprising:

irregularities repeatedly formed on the surface of said stamping die along a first direction; and

irregularities repeatedly formed on the surface of said stamping die along a second direction crossing said first

formed with opening portions at suitable intervals, and emitting ultraviolet rays to said stamping film through said mask; a second heating process of heating said stamping film after said ultraviolet ray emitting process; a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along a direction different from said optional direction in said first stamping process, on said stamping film; and a process of pressing said stamping die on said film after said second stamping process, thereby stamping the surface shape of said stamping film on said stamping stamping die. A method of forming an alignment film for a liquid 15. crystal element, comprising: a first heating process of heating an alignment film preliminary layer made of a thermoplastic ultraviolet ray hardening resin formed on a substrate; a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along an optional direction, on said alignment film preliminary layer; a ultraviolet ray emitting process of disposing a mask - 79 -

formed with opening portions at suitable intervals, and emitting ultraviolet rays to said alignment film preliminary layer through said mask; a second heating process of heating said alignment film preliminary layer after said ultraviolet ray emitting process; and a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along a direction different from said optional direction in said first stamping process, on said alignment film preliminary layer. A method of manufacturing a stamping die for forming an 16. alignment film for a liquid crystal element, comprising: a first heating process of heating a stamping film made of a thermoplastic ultraviolet ray hardening resin formed on a substrate; a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along an optional direction, on said stamping film; a ultraviolet ray emitting process of disposing a mask formed with opening portions at suitable intervals, and emitting ultraviolet rays to said stamping film through said mask; 80 -

a second heating process of heating said stamping film after said ultraviolet ray emitting process; and a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along a direction different from said optional direction in said first stamping film. process, on said A method of manufacturing a stamping die for forming an 17. alignment film for a liquid crystal element, comprising: a first heating process of heating a stamping film made of a thermoplastic ultraviolet ray hardening resin formed on a substrate; a first stamping process of pressing, a single domain stamping die on the surface of which a plurality of irregularities are repeatedly formed along an optional direction, on said stamping film; a ultraviolet ray emitting process of disposing a mask formed with opening portions at suitable intervals, and emitting ultraviolet rays to said stamping film through said mask; a second heating process of heating said stamping film after said ultraviolet ray emitting process; and a second stamping process of pressing, a single domain stamping die on the surface of which a plurality of - 81 -

irregularities are repeatedly formed along a direction different from said optional direction in said first stamping process, on said stamping film; wherein the surface shape is formed on said stamping die by electro-casting using said stamping film after said stamping process as an original template. 18. A stamping apparatus used for pressing a die member having an irregular pattern on an alignment film preliminary layer on a substrate thereby stamping the irregular pattern on the upper surface of said alignment film preliminary layer, comprising: a press base body made of a rigid body; an elastic member disposed so as to face to said press - 1 base body; and a sheet-like die member provided on the side not facing to said press base body of said elastic member. 19. A stamping apparatus according to claim 18, wherein said elastic member is mounted on the surface of said press base body, and said die member is mounted on the surface of said elastic member.

- 20. A stamping apparatus for forming an irregular pattern on an alignment film according to claim 18 or 19, wherein said press base body is formed in a flat shape.
- 21. A stamping apparatus for forming an irregular pattern

on an alignment film according to 18 or 19, wherein said press base body is formed in a roller shape. A stamping apparatus according to any of claims 18 to 22. 21, wherein said die member is formed to a thickness in the range of from 0.001 mm to 0.2 mm. A stamping apparatus according to any of claims 18 to 23. 22, wherein a coating layer made of gold, gold alloy, copper or copper alloy is formed on the surface of said die member. A liquid crystal element substantially as 24. hereinbefore described with reference to, and as illustrated by, the accompanying drawings. A method of manufacturing a liquid crystal 25. element substantially as hereinbefore described with 5 reference to, and as illustrated by, the accompanying drawings. A stamping die substantially as hereinbefore 26. described with reference to, and as illustrated by, the accompanying drawings. 10 A method of manufacturing a stamping die 27. substantially as hereinbefore described with reference to, and as illustrated by, the accompanying drawings. A method of forming an alignment film for a 28. liquid crystal element substantially as hereinbefore 15 described with reference to, and as illustrated by, the accompanying drawings. A stamping apparatus for forming a pattern on an 29. alignment film substantially as hereinbefore described with reference to, and as illustrated by, the accompanying 20 drawings. - 83 -





**Application No:** 

GB 9512661.1

Claims searched: 1 to 10

Examiner:

Mr.G.M Pitchman

Date of search: 21 September 1995

Patents Act 1977 Search Report under Section 17

#### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): G2F(FCT)

Int Cl (Ed.6): G02F1/1337

Other: ONLINE: EDOC WPI JAPIO

#### Documents considered to be relevant:

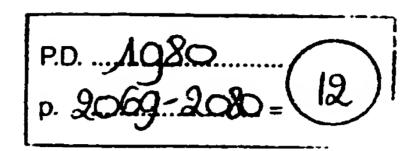
Category	Identity of document and relevant passage		Relevant to claims
Y	DE 4213802	(ALPS ELECTRIC)-see abstract and page 3 lines 46 to 51	1 to 10
Y	US 5280375	(MATSUSHITA)-see abstract	1 to 10
Y	Patent Abstracts	of Japan Section P:P-177 Vol. 7 No.42 &JP 57192926	1 to 10

& Member of the same patent family

- A Document indicating technological background and/or state of the art.
- P Document published on or after the declared priority date but before the filing date of this invention.
- E Patent document published on or after, but with priority date earlier than, the filing date of this application.

X Document indicating lack of novelty or inventive step

Y Document indicating lack of inventive step if combined with one or more other documents of same category.



XP-000892038

# Mechanically Bistable Liquid-Crystal Display Structures

ROBERT N. THURSTON, SENIOR MEMBER, IEEE, JULIAN CHENG, AND GARY D. BOYD, FELLOW, IEEE

Abstract—This paper discusses two types of mechanically bistable liquid-crystal display structures, a previously reported type [2], [3] called vertical-horizontal, and a second type, called horizontal-horizontal. In both of them, the director configuration is planar. They are distinguished by the orientation of the director plane, which is perpendicular to the major surfaces of the device in the type called vertical-horizontal, and parallel in the type called horizontal-horizontal. In both types, the bistable states may be differentiated optically by use of a polarizer and dichroic dye, and switching is accomplished electrically by exploiting the dielectric anisotropy of the ordered liquid crystal states. We show exculations of the director configurations, their energy, and optical contrast of the bistable states.

The bistable states are topologically distinct, so that the switching transitions are necessarily discontinuous in character. The movement of disclinations governs the switching process, and their detachment forms the basis of stability.

Manuscript received February 20, 1980; revised May 27, 1980. The authors are with Bell Laboratories, Holmdel, NJ 07733.

#### I. INTRODUCTION

are potentially useful as elements in displays. Although conventional liquid-crystal twist cells [1] have found important applications, they lack the desirable feature of power-off memory that mechanical bistability can provide. A mechanically bistable structure is one in which the liquid-crystal director can assume either of two different ordered stable configurations of equal or nearly equal energy. Displays based on mechanical bistability have been disclosed by Boyd, Cheng, and Ngo [2], [3] and by Berreman and Heffner [4].

A toggle switch is an example of a mechanical system that is bistable. The switch stays in either position without having to be held. Both equilibrium configurations are stable, since an energy barrier must be overcome to pass from one to the other.

0018-9383/80/1100-2069\$00.75 © 1980 FEEE

There is another type of liquid-crystal bistability, called thermodynamic, in which two different stable (or long-lived metastable) states result from the application of different thermal or electrical histories [5]-[7]. In a display described by Tani et al. [8], appropriate choice of the voltage history, applied to a nematic-cholesteric mixture, produces either an amost-transparent spiral texture or a scattering texture, both with voltage off. Thermodynamic bistability involves an order-disorder transition, whereas the mechanical bistability of the present paper involves a transition between two ordered states of minimum energy separated by an energy barrier.

Equilibrium configurations of different types and their stability in a twist cell with tilted boundary conditions have been studied [9]-[12]. Scheffer [9] and Miyaji et al. [10] found a critical twist angle for which a symmetrically tilted configuration with twist >90° has the same energy as an antisymmetric configuration with the opposite twist <90°. Porte and Jadot [11] found the surface tilt angle at which a 180°-twisted configuration is spontaneously transformed into a nontwisted configuration.

The work of Porte and Jadot [11] shows that both non-twisted and 180°-twisted configurations are achievable, depending on the boundary conditions and material parameters. The nontwisted state is achieved when the director orientation at the boundary is closer to the normal than some critical angle which depends on the elastic constants. As noted earlier [2], the nontwisted and 180°-twisted states are topologically equivalent (in the sense that one can be continuously deformed into the other) and they have very similar optical and switching properties.

Leaving aside the interesting possibilities of twisted states for a separate treatment, we consider in this paper only configurations in which the director lies in a plane either parallel or perpendicular to the major surfaces of the liquid-crystal cell (planar configurations).

The equilibrium equation for planar configurations, derived in the Appendix, reduces to Laplace's equation in the director angle when the bend and splay elastic constants are assumed equal as an approximation [13]. The Appendix (subsection B and Fig. 18) demonstrates the excellence of this approximation. Hence, throughout the remainder of the paper, by solutions of the equilibrium equation, we mean solutions of Laplace's equation. Different solutions corresponding to the same physical boundary conditions occur because the same physical boundary condition can be expressed by a multiplicity of director angles. For example, changing the director angle along part of the boundary by  $n\pi$  (n = integer) leaves the physical boundary condition unchanged, but changes the configuration and the corresponding solution. The boundary condition at a surface is the local orientation of the director with respect to the surface, specified by the angle  $\theta$  between the director and the surface normal, and an azimuth angle  $\phi$ measured in the plane of the surface. The local orientation at the surface of a liquid-crystal cell may be affected by the nature of the surface, surface treatment, the action of electric

or magnetic fields, and the direction of flow at the time of initial contact of the nematic liquid crystal with the solid surface when the cell is filled.

Some experiments described by Cheng and Boyd [14] suggest that the interaction of interfacial molecules with the substrate is very strong, and that their orientation at the time of initial contact with the surface is strongly pinned. This produces a surface orientational bias which may be governed by external fields, hydrodynamic shear flow, surface defects and inhomogeneity, and surface topography (such as grating structures). Biased surface alignment is not generally susceptible to reorientation by external fields.

When cells are filled with the liquid crystal in the isotropic phase, the flow direction is immaterial. In this case, it appears that the orientation at the time of the isotropic-nematic phase transition determines the azimuth angle. The orientation during the phase transition can be the resultant effect of applied fields acting through the developing dielectric or magnetic anisotropy, and topology acting to align the director in such a way as to minimize the developing elastic energy.

One way to control the surface tilt is by oblique evaporation of  $SiO_x$ ,  $MgF_2$ ,  $TiO_2$ , or other materials. Alignment either parallel or at an angle to the surface is possible by controlling the angles of bombardment, and the sequence of steps and the film thicknesses in multiple evaporations [15]-[21].

Another way to determine a specified tilt angle has been suggested by Berreman [22]. Adjacent narrow stripes of alternating perpendicular and parallel surface alignment cause the director a short distance away from the surface to assume an average tilt angle that depends on the widths of the regions and their anchoring energy. The average tilt can be either left or right. Similar ideas have been proposed by Meyer [23].

Fig. 1 shows an interesting case of bistability in a liquid crystal of infinite extent bounded by a plane. Here the left half of the surface favors parallel alignment and the right half perpendicular alignment. With  $\beta$  as the coordinate angle measured clockwise from the surface normal, there are two exact solutions of Laplace's equation for the director angle  $\theta(\beta)$  of the form  $\theta = S\beta + \theta_0$ , one with  $S = -\frac{1}{2}$ , in which  $\theta(0) = \pi/4$ , and one with  $S = +\frac{1}{2}$ , in which  $\theta(0) = -\pi/4$ . This bistability with only two regions on the surface reminds one of Berreman's discovery of left or right tilt produced by many small regions of alternating parallel or perpendicular alignment [22].

This paper discusses two major types of mechanically bistable planar structures. These are distinguished by the orientation of the director plane, which is parallel to the substrates for horizontal-horizontal bistability and perpendicular to them for vertical-horizontal bistability. In either case, the bistable states may be optically differentiated by incorporating pleochroic dyes in the liquid-crystal host and exploiting the pronounced molecular dichroism of the dyes [24], [25]. The guest pleochroic dye molecules align their axes parallel to the local director of the host liquid crystal, and have the property of strongly absorbing light polarized along their axes, but not light polarized normal to their axes. Switching, in both types

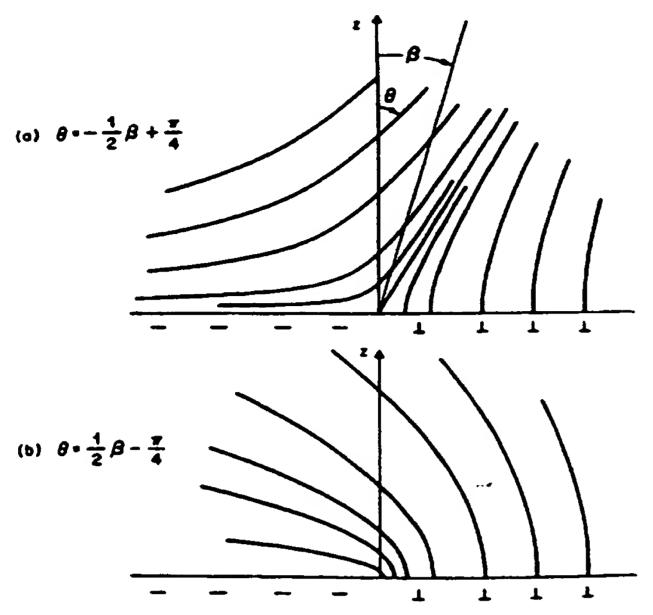


Fig. 1. Bistability on a single surface in a liquid crystal of infinite extent. In both (a) and (b) the boundary conditions are identical: the left half of the surface has parallel alignment and the right half perpendicular alignment. The two solutions of the form  $\theta = S\beta + \theta_0$  have the same energy, but the tilt along a line drawn vertically upward through the disinclination is 45° in (a) and -45° in (b).  $\beta =$  polar coordinate,  $\theta =$  director angle, both measured clockwise from the vertical.

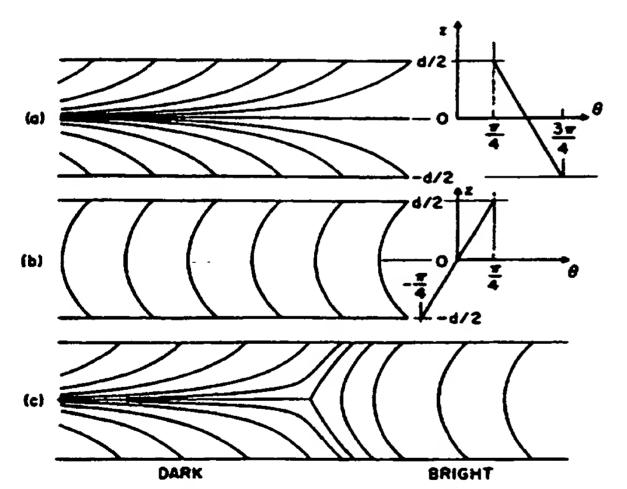


Fig. 2.  $\theta$  versus z and director lines for a single-tilt bistable structure. The boundary conditions at z = d/2 are physically identical in the two cases. Such tilt boundary conditions can be realized by evaporation at an angle. (a)  $\theta(z) = -\pi z/2d + \pi/2$ . (b)  $\theta(z) = +\pi z/2d$ . (c) Domains like (a) and (b) separated by a disinclination of strength S = -1/2. With positive dielectric anisotropy, a vertical field in (c) would cause growth of the predominantly vertical domain through leftward motion of the disclination. With a pleochroic dye dissolved in the liquid crystal, vertically transmitted light that is horizontally polarized in the plane of the figure is strongly absorbed in the "horizontal" domain to the left of the disclination but not in the "vertical" domain to the right.

of structures, is accomplished electrically by using liquid crystals having a large positive dielectric anisotropy, whose molecules are thus constrained to lie parallel to the local field direction. Switching of these bistable structures requires the motion of disclinations, whereas a different type of elastic bistability described by Berreman and Heffner [4] does not.

## II. STRUCTURES WITH VERTICAL-HORIZONTAL BISTABILITY

## A. Uniform Tilt on Upper and Lower Surfaces (Single-Tilt Geometry)

Fig. 2 shows a liquid-crystal structure in which boundary conditions prescribing roughly 45° tilt on the upper and lower surfaces of the liquid-crystal cell were created in some manner such as by oblique evaporation [21]. The liquid crystal will remain in either the horizontal state of Fig. 2(a) or the vertical state of Fig. 2(b). When the tilt angle is 45°, the horizontal and vertical states can be shown to have equal configuration energies if the bend and splay elastic constants are equal. Fig. 2(c) illustrates an essential feature of the switching between the configurations of (a) and (b). The boundary between the two domains contains a disclination of strength  $S = -\frac{1}{2}$ . Because of the dielectric or magnetic anisotropy of the ordered liquid-crystal states, an applied field can favor one domain over the other, and cause one domain to grow at the expense of the other through motion of the disclination.

The two states illustrated in Fig. 2(c) can be distinguished by dissolving a pleochroic dye in the liquid crystal [24], [25]. Vertically transmitted light that is horizontally polarized in the plane of the figure will then be strongly absorbed to the left of the disclination but not to the right of it.

When the director angle depends on only a single rectangular coordinate, as in Fig. 2(a) or (b), the solution of Laplace's equation is simply

$$\theta(z) = m(z - z_0). \tag{1}$$

The director lines for such a one-dimensional situation, obtained by integration of the equation

$$\frac{dx}{dz} = \tan \theta \tag{2}$$

are given by

$$x = x_0 + \frac{1}{m} \ln |\sec [m(z - z_0)]|.$$
 (3)

Fig. 3 is a plot of this equation, which is a "universal" director line for a one-dimensional variation of tilt. The director lines for Fig. 2(a) lie between the ordinate values 1 and 3 on Fig. 3, and for Fig. 2(b) between 3 and 5. Director lines for other values of tilt on the upper and lower surfaces may be obtained by choosing an appropriate segment of the curve in Fig. 3.

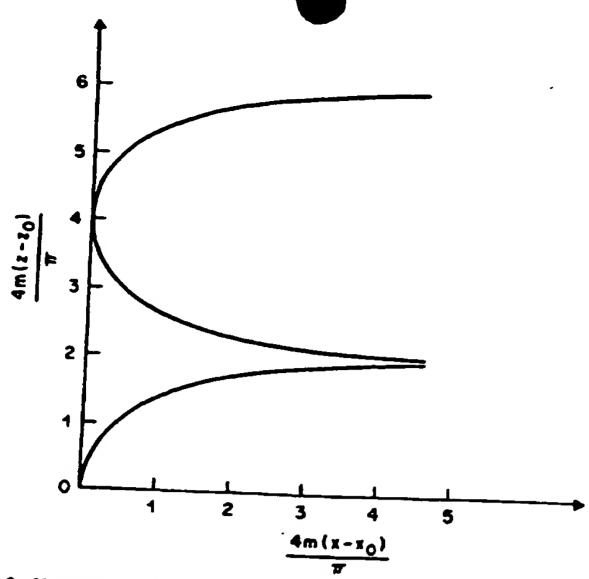


Fig. 3. Universal director line for one-dimensional variation of tilt. When the director angle  $\theta(z)$  is linear in z, given by  $\theta(z) = m(z - z_0)$ , the director line x(z), obtained by integration of  $dx/dz = \tan \theta$ , is  $x(z) = x_0 + (1/m) \ln |\sec \theta(z)|$ . In such a one-dimensional situation, with no twist and elastic constants assumed equal, all possible director lines are segments of the illustrated curve.

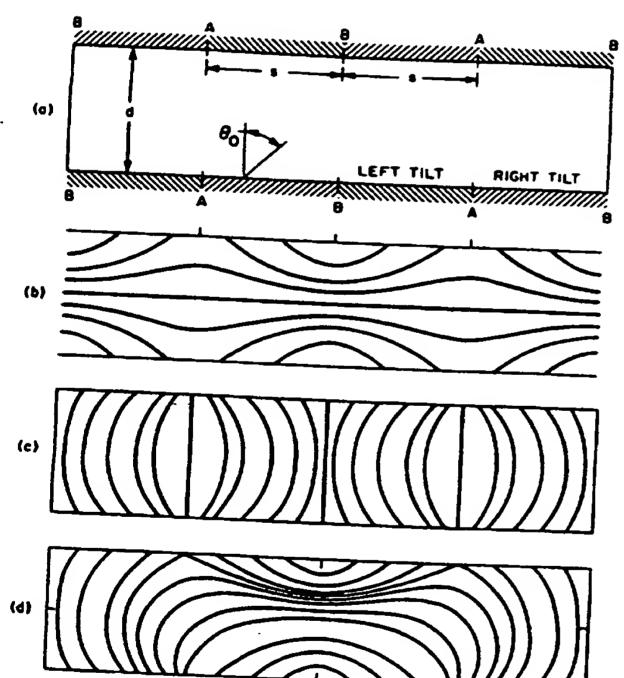


Fig. 4. A bistable liquid-crystal structure. Part (a) illustrates spatially periodic tilt boundary conditions on the upper and lower surfaces (double-tilt geometry). The tilt is roughly 45°, changing by 90° at points A and B, such that the tilt is away from A, toward B. Parts (b) to (d) show director line configurations with the central cell ABA in (b) a horizontal state with a horizontal state to both left and right, (c) a vertical state with a vertical state to both left and right, and (d) a horizontal state with a vertical state to both left and right.

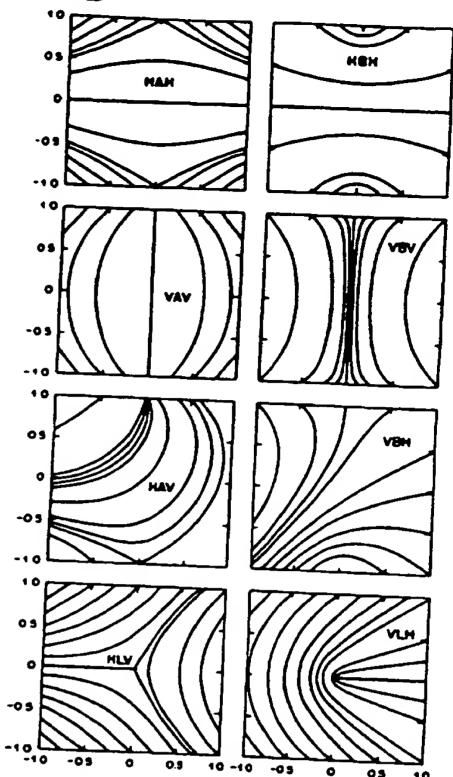


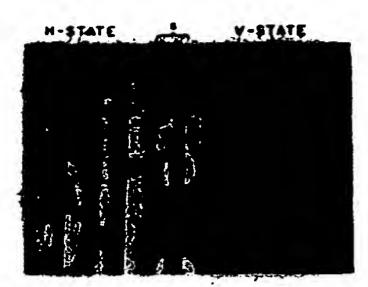
Fig. 5. Director lines in the neighborhood of domain boundaries for  $\theta_0 = 45^\circ$ . A and B refer to the types of junctions in the double-tilt structure of Fig. 4. The bottom pair of pictures applies to the single-tilt structure of Fig. 2.

## B. Alternating Tilt on Upper and Lower Surfaces (Double-Tilt Geometry)

Fig. 4 shows another liquid-crystal structure that we have experimentally demonstrated to be bistable. The boundary condition illustrated in Fig. 4(a), with a roughly 45° tilt, left and right in adjacent regions of equal width, was created by oblique evaporation onto the substrates that comprise the upper and lower surfaces of the liquid-crystal cell. In this structure, bistability means that the liquid crystal will remain in either the horizontal state of Fig. 4(b) or the vertical state of Fig. 4(c). As in Fig. 2, the horizontal and vertical states have equal configuration energies when the tilt angle is 45°.

It is interesting to see how the director lines look near the "A" and "B" junctions of Fig. 4, and near a vertical-horizontal transition in Fig. 2. Fig. 5 shows the results of our calculations for the six physically different domain boundaries of Fig. 4 and the two of Fig. 2.

Switching from a horizontal to a vertical state can be accomplished by applying a vertical electric field at a low frequency where the liquid crystal has positive dielectric anisotropy. Vertical-to-horizontal switching is accomplished by a transverse field. A vertical field at a higher frequency where the anisotropy in certain materials can be negative [26] produces interesting effects, but not complete vertical-to-horizontal switching.



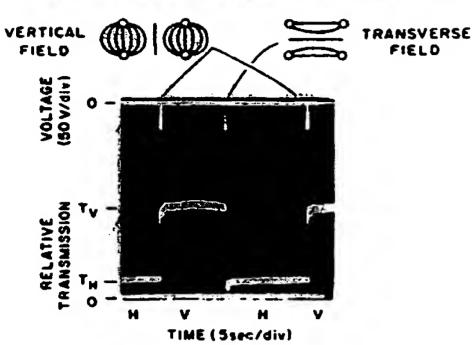


Fig. 6. Photograph showing contrast between horizontal and vertical domains under illumination by light horizontally polarized in the plane of the paper. The horizontal domain appears dark and the vertical domain bright because of the differential absorption provided by the pleochroic dye. (a) Optical contrast of double-tilt device, showing the blue horizontal and white vertical states. (b) Relative optical transmission (at  $\lambda 550$  nm) of the horizontal and vertical states and their electrical switching using interdigital electrodes. This illustrates contrast and memory in a cell consisting of an E8/D5 mixture (materials from EM Laboratories), with  $s = d = 50 \mu m$ . (d = cell depth; s = spacing of A and B junctions in Fig. 4.)

Optical contrast between the vertical and horizontal states is achieved by mixing a pleochroic dye with the liquid crystal, as discussed in connection with Fig. 2. Vertically transmitted light that is horizontally polarized in the plane of the figure is then strongly absorbed by the horizontal state (which appears dark) but not by the vertical state.

Fig. 6 is a photograph illustrating the contrast between vertical and horizontal states.

#### III. OPTICAL TRANSMISSION CALCULATIONS

We wish to calculate the relative brightness of the vertical and horizontal states, and its dependence on the absorption coefficient and tilt angle at the upper and lower surfaces.

Light transmission through a liquid crystal that contains a pleochroic dye is described by the classical theory of electromagnetic propagation in a lossy, anisotropic medium [27, sec. 14.6, pp. 708-718]. In the present application, a polarizer blocks the ordinary ray, leaving only the extraordinary ray, whose propagation velocity and attenuation (in a homogeneous uniaxial crystal) are described by the equation [27, eq. 14.6(20), p. 711]

$$\frac{1}{\widehat{n}^2} = \frac{\cos^2 \theta}{\widehat{n}_c^2} + \frac{\sin^2 \theta}{\widehat{n}_c^2} \tag{4}$$

where  $\theta$  is the angle between the propagation direction and the

optic axis defined by the liquid-crystal director,  $\hat{n}$  is the complex index of refraction, and  $\hat{n}_o$  and  $\hat{n}_e$  its ordinary and extraordinary complex values. With

$$\hat{n} = n + i\alpha c/\omega \tag{5}$$

the complex exponential representation of the space-time dependence of a wave propagating in the z direction is

$$\exp\left[i\omega\left(\frac{\hat{n}z}{c}-t\right)\right] = \exp\left[-\alpha z + i\omega\left(\frac{nz}{c}-t\right)\right] \tag{6}$$

which shows that  $\alpha$  is the attenuation factor. The separation of real and imaginary parts in (4) yields two equations which can be solved simultaneously for n and  $\alpha c/\omega$  in terms of  $\theta$  and the real and imaginary parts of  $\hat{n}_o = n_o + i\alpha_1 c/\omega$  and  $\hat{n}_e = n_e + i\alpha_1 c/\omega$ .

While the angle dependence of the loss that results from the exact equation (4) is easily programmed for computer calculations, we use a simpler model to see the essentials. The physical property responsible for the optical contrast between vertical and horizontal states is not the dielectric anisotropy, of course, but the absorption anisotropy. If for simplicity we assume  $n = n_o = n_e$ , and in addition assume that the attenuation per radian of phase shift is small compared with unity  $(\alpha \lambda/2\pi \ll 1)$  so that powers of  $(\alpha c/\omega n)$  higher than the first can be neglected, then (4) yields

$$\alpha = \alpha_1 \cos^2 \theta + \alpha_1 \sin^2 \theta. \tag{7}$$

Since a typical liquid-crystal cell is several tens of wavelengths thick, we can obtain reasonable results by assuming that the wave in each infinitesimal layer of thickness dz is the same as in a homogeneous medium in which the optic axis has the constant direction given by the local director angle  $\theta(x, z)$ . For a wave propagating in the z direction, the differential equation for the decay of a field amplitude such as E is

$$\frac{dE}{F} = -\alpha \, dz \tag{8}$$

from which the decay of amplitude in a cell of thickness d is  $\exp(-Q\alpha_{\parallel}d)$  where

$$Q \equiv \frac{1}{\alpha_{\parallel} d} \int_{-d/2}^{d/2} \alpha \, dz. \tag{9}$$

The transmitted intensity, relative to T = 1 for perfect transmission, is then

$$T = \exp\left(-2Q\alpha_{\parallel}d\right). \tag{10}$$

In the one-dimensional situations pictured in Fig. 2(a) or (b)  $\theta$  is linear in z, and if  $\theta_0$  denotes the magnitude of the tilt angle with respect to the normal at the upper and lower surfaces where  $z = \pm d/2$ ,  $\theta(z)$  is given by

$$\theta_{V}(z) = \pm 2\theta_{0} z/d \tag{11}$$

in the vertical state and

$$\theta_H(z) = \frac{\pi}{2} \mp (\pi - 2\theta_0)z/d \tag{12}$$

in the horizontal state. With  $\theta_0$  between 0 and  $\pi/2$ , the upper and lower signs describe leftward-tilting and rightward-tilting boundaries, respectively. For vertical propagation, the director angle measured from the light propagation direction is the same as the angle measured from the z axis, and the  $\theta$  of (4) and (7) is the same as the  $\theta$  of (11) and (12). From (7), (9), (11), and (12), the parameter Q for the vertical and horizontal states is

$$Q_{\nu} = \frac{\alpha_{\perp}}{\alpha_{\parallel}} + \frac{\alpha_{\parallel} - \alpha_{\perp}}{2\alpha_{\parallel}} \left( 1 - \frac{\sin 2\theta_{0}}{2\theta_{0}} \right) \tag{13}$$

$$Q_{H} = \frac{\alpha_{\parallel}}{\alpha_{\parallel}} + \frac{\alpha_{\parallel} - \alpha_{\perp}}{2\alpha_{\parallel}} \left(1 + \frac{\sin\left(\pi - 2\theta_{0}\right)}{\pi - 2\theta_{0}}\right). \tag{14}$$

The transmitted intensities through the horizontal and vertical states  $T_H$  and  $T_V$  are given by (10) with  $Q = Q_H$  and  $Q_V$ , respectively.

Two reference values of T of interest are  $T_{\parallel}$  for the director everywhere horizontal, and  $T_{\perp}$  for the director everywhere vertical. The first case has  $\alpha \equiv \alpha_{\parallel}$  so that

$$Q_{\parallel} \equiv Q_{H}|_{\theta_{0} = \pi/2} = 1$$

$$T_{\parallel} \equiv T_{H}|_{\theta_{0} = \pi/2} = \exp(-2\alpha_{\parallel}d). \tag{15}$$

The second case has  $\alpha \equiv \alpha_1$  so that

$$Q_{\perp} \equiv Q_{V}|_{\theta_{0} = \pi/2} = \alpha_{\perp}/\alpha_{\parallel}$$

$$T_{\perp} \equiv T_{V}|_{\theta_{0} = \pi/2} = \exp(-2\alpha_{\perp}d). \tag{16}$$

Fig. 7 shows  $T_{\parallel}$ ,  $T_{H}$ ,  $T_{V}$ , and  $T_{H}/T_{V}$  versus  $\alpha_{\parallel}d$  with  $\alpha_{\perp}=0$  and the boundary tilt angle  $\theta_{0}=45^{\circ}$ . Fig. 8 shows  $T_{H}$ ,  $T_{V}$ , and  $T_{H}/T_{V}$  versus  $\theta_{0}$ , still for  $\alpha_{\perp}=0$ , and for the particular value  $\alpha_{\parallel}d=1.8$ , which is the value that provides a contrast ratio  $T_{V}/T_{H}$  of 10 when  $\theta_{0}=45^{\circ}$ . It can be seen that the contrast ratio varies slowly with  $\theta_{0}$ , and is best at  $45^{\circ}$ .

#### IV. HORIZONTAL-HORIZONTAL BISTABILITY

#### A. Motivation and Description

We now consider displays that use horizontal-horizontal bistability, in which the director lies in a plane parallel to the major surfaces of the cell. Contrast is obtained by making the director either parallel or perpendicular to the polarization of the incident light.

Horizontal-horizontal bistability has several appealing features. From the viewpoint of fabrication, complex surface topography can be simply and accurately implemented with modern photolithography, whereas it is not always possible to produce an arbitrary surface topography reliably by oblique film deposition. Obliquely deposited films do not always retain their integrity through successive fabrication steps. In addition, it is easier to define the pinning sites and boundary conditions in horizontal-horizontal configurations.

Balanced against these possible advantages is the fact that strong interfacial interactions at the liquid crystal-substrate interface may prevent switching. The larger question regarding the nature of these interactions and how they can be minimized is a fertile field of investigation at present poorly under-

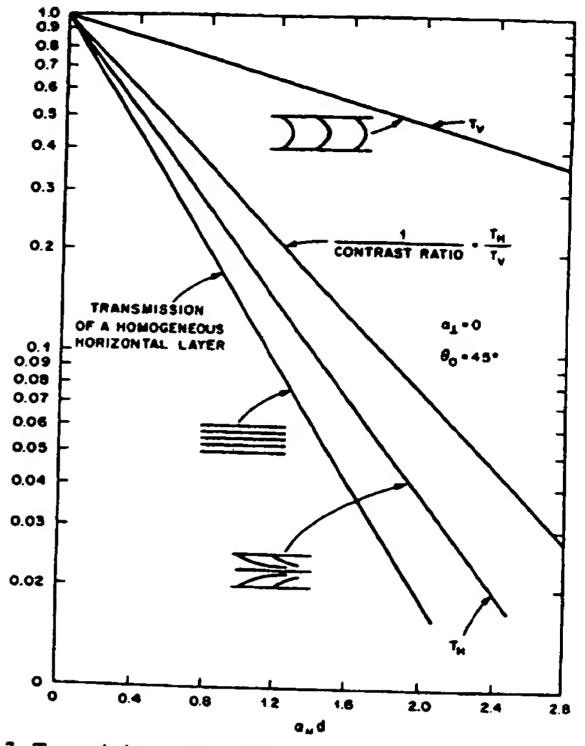


Fig. 7. Transmission versus  $\alpha_{\parallel}d$  for boundary tilt  $\theta_0 = 45^{\circ}$ . From top to bottom the curves show 1) transmission through the vertical state  $T_V$ , 2) the ratio  $T_H/T_V$ , 3) transmission in the horizontal state  $T_H$ , and 4) the transmission through a homogeneously oriented horizontal layer.

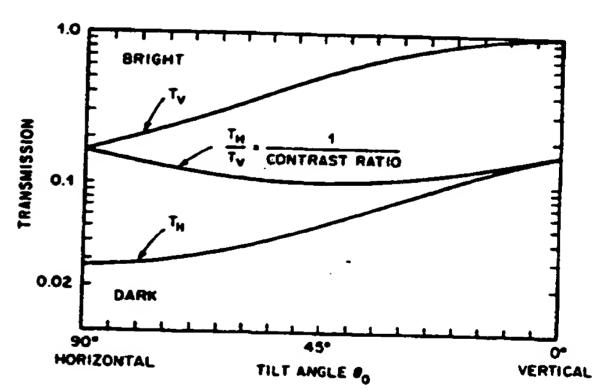


Fig. 8. Transmission versus boundary tilt  $\theta_0$  for  $\alpha_{\parallel}d=1.8$ . From top to bottom the three curves show  $T_V$ ,  $T_H/T_V$ , and  $T_H$ . The maximum contrast ratio is at  $\theta_0 = 45^\circ$ .

stood. In the following discussion, we assume that a "slippery surface" is possible.

Fig. 9 shows a structure that provides a horizontal-horizontal bistability with the dominant direction along one of the two diagonals of the enclosed square. Here the azimuth in the region surrounding a square is defined photolithographically by gratings [28], [14], on the upper and lower surfaces. In-

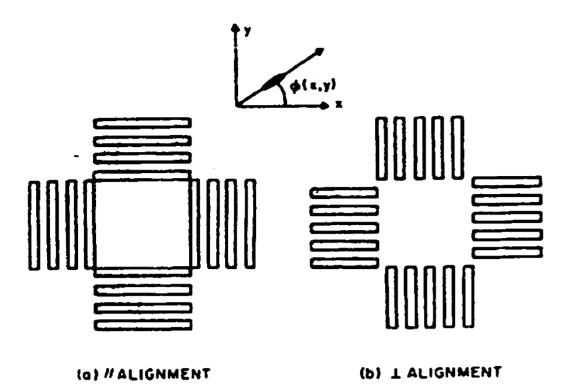


Fig. 9. Square regions defined by grating boundaries giving (a) parallel or (b) perpendicular alignment conditions.

side the square, the surface treatment is assumed to be such that the interaction of the surface with the liquid crystal causes alignment parallel to the surface but with no preferred azimuth. The liquid-crystal molecules inside the square column are imagined free to reorient themselves under the influence of applied fields and the boundary conditions imposed by the aligned molecules in the region surrounding the square. As illustrated in Fig. 9(a) and (b), the gratings can be arranged to provide alignment either parallel to the edges of the square or perpendicular to them.

## B. Director Lines for Horizontal-Horizontal Bistability in a Square

When boundary conditions are imposed at the edges of a square, the director configuration inside the square is determined (under the assumption of equal bend and splay elastic constants) by the solution of Laplace's equation. For parallel or perpendicular boundary conditions, the configurations of lowest energy are the bistable diagonal states whose director lines are illustrated in Fig. 10(a) and (b). The bistability follows simply from the fact that the straight director line can fall along either diagonal of the square. The configurations of next lowest energy are the fourfold degenerate ones shown in Fig. 10(c) and (d). Each of these different configurations (and each of their equal-energy mates) is a unique solution of Laplace's equation for specified boundary values. The different solutions corresponding to the same physical boundary conditions are obtained by different resolutions of the ±180° ambiguity in the value of the director angle at a boundary.

### C. Energy Difference Between the Lowest and Next Lowest States

It is straightforward to calculate the energy difference  $\delta G$  of the two lowest states for a rectangle of sides (a, b). With  $\phi$  calculated by the classical method of separation of variables the result is

$$\delta G = 4\pi^2 kd \sum_{n=0}^{\infty} \frac{1}{b_n \sinh{(ab_n/b)}}$$
 (17)

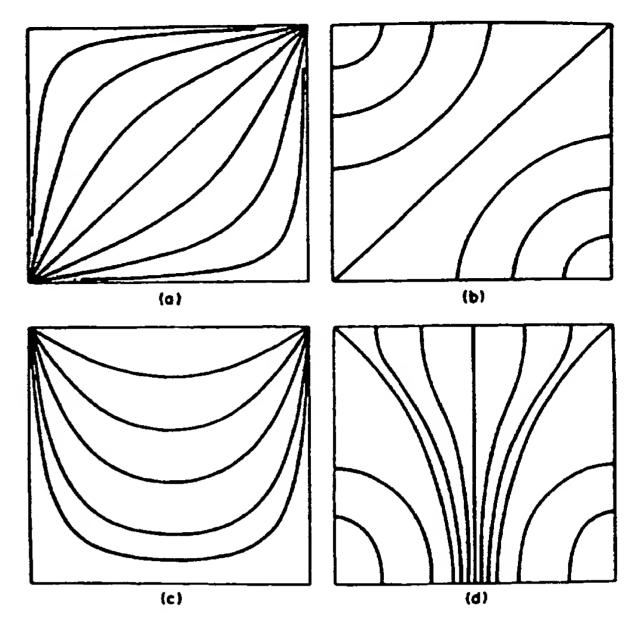


Fig. 10. Director lines for states in a square. (a) and (b) Lowest states with parallel and perpendicular boundary conditions, respectively. (c) and (d) Second states with parallel and perpendicular boundary conditions, respectively.

where  $b_n = (2n+1)\pi$ , k is the elastic constant, and d the cell depth. When a/b is small, the configurations of Fig. 10(c) or (d) are highly distorted as compared with Fig. 10(a) or (b), and the energy difference is large. On the other hand, the energy difference tends to zero with increasing a/b. For a square,  $\delta G = 1.088 \ kd$ .

This energy difference is, however, too small to provide a preponderance of the diagonal over the parallel states. With a typical dimension of  $a = b = 50 \,\mu\text{m}$ , and  $d = 25 \,\mu\text{m}$ , we find an energy difference of  $10^{-4}$  ergs/cm<sup>2</sup>, significantly smaller than the anchoring energy of many surfaces. Thus the two diagonal and four parallel states comprise a set of nearly degenerate local minima in elastic energy. These states are separated by a continuum of intermediate states with a higher singularity content, as shown in Fig. 11. Switching may consist of the motion of one or more of these excess singularities along the periphery of the square. The barrier energy is approximately that of the excess singularities, or, with disclination core radius  $r_0$  [29, eq. (4.7), p. 131]

$$\delta G = \pi k S^2 d \cdot \ln \left( \frac{a}{r_0} \right), \quad S = 1.$$
 (18)

The states are thus pinned by the corners of the square. Optically the square has four distinct states, two diagonal ones and two parallel to the edges.

#### D. Applications of Bistability in a Square

A straightforward application of the bistability in a square is illustrated in Fig. 12 where boundary conditions on both the

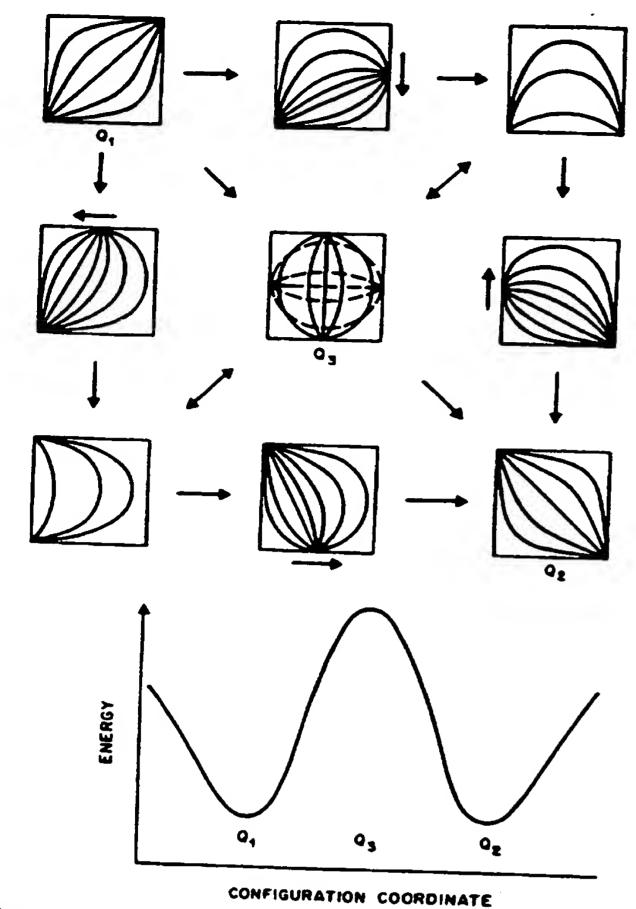


Fig. 11. Diagonal and parallel states, and intermediate states of higher singularity content for the internal states of a square.

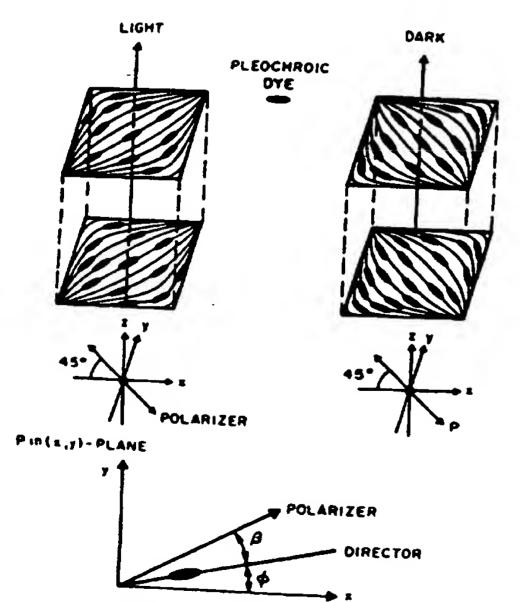


Fig. 12. Optical differentiation of the degenerate diagonal states of a square.

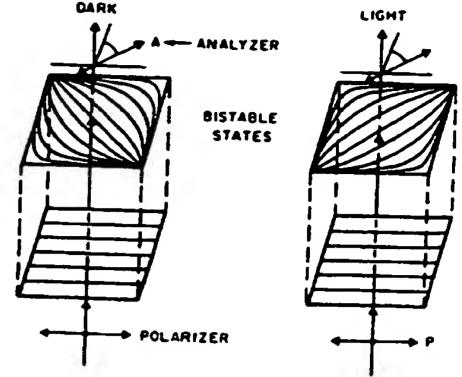


Fig. 13. Use of the bistable states of a square in a twist cell. The azimuth at the lower surface is assumed to be fixed while that at the upper surface is switched between the bistable diagonal states.

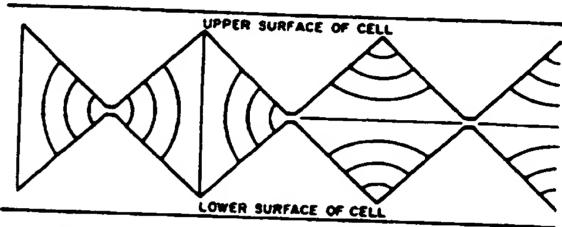


Fig. 14. Achievement of vertical-horizontal bistability with perpendicular boundary conditions on all surfaces. In this case, the plane of the figure is a vertical cross section of the liquid-crystal cell. V-bottomed indentations in the upper and lower surfaces of the cell provide square boundaries for the liquid crystal.

upper and lower surfaces result in the indicated two-dimensional situation. Optical contrast between the two diagonal states, obtained by use of a pleochroic dye, is discussed in the next subsection.

Another bistable structure based on the bistability of the two diagonal states of a square is the twist cell shown in Fig. 13 in which the alignment at one surface is fixed by a grating and the opposite surface is in one of the bistable states. Good optical differentiation of the states in this case would appear to require both a polarizer and an analyzer as illustrated.

The bistability of the diagonal states in a square with perpendicular boundary conditions also suggests another structure for achieving a horizontal-vertical bistability resembling that discussed in Section II-B. Instead of the alternating tilt boundary conditions of Fig. 4(a), the upper and lower surfaces may be formed with 90° V-bottomed indentations arranged such that the space for the liquid crystal is essentially a series of channels of square cross section. As illustrated in Fig. 14, the diagonal states in these squares are then either horizontal or vertical, and contrast can be achieved with a pleochroic dye as already discussed. The resemblance to the configurations of Fig. 4 is most striking if the top and bottom corners of the squares are imagined to be cut off by horizontal planes on which the alternating tilt boundary conditions are imposed.

### E. Optical Contrast with Horizontal-Horizontal Bistability

In the two-dimensional situation of Fig. 12, vertically transmitted light can be resolved into an extraordinary ray polarized

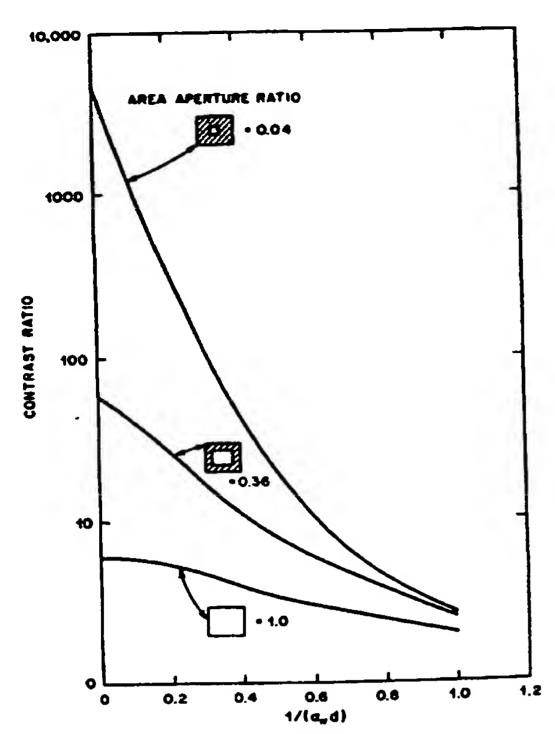


Fig. 15. Contrast ratio versus  $(\alpha_{\parallel}d)^{-1}$  for light transmission through the cell of Fig. 12, with  $\alpha_{\perp} = 0$ .

along the optic axis (director) and an ordinary ray. If  $\beta$  denotes the angle between the polarizer direction and the director, the transmitted intensity of the elliptically polarized emergent light is (in the plane wave approximation) proportional to

$$I(x, y) = e^{-2\alpha \eta d} \cos^2 \beta(x, y) + e^{-2\alpha \eta d} \sin^2 \beta(x, y)$$
 (19)

where d is the cell thickness. Let subscripts 1 and 2 refer to the diagonal configurations with the director predominantly along the polarizer and perpendicular to it, respectively. Then state 1 is dark and 2 is bright. From the boundary conditions for the two cases,  $\phi_2 = 180^{\circ} - \phi_1$ . With the polarizer set along a square diagonal

$$\cos^2 \beta_2 = \sin^2 \beta_1 \qquad \sin^2 \beta_2 = \cos^2 \beta_1.$$
 (20)

Defining

$$T_{j} = \int \int I_{j}(x,y) dx dy, \quad j = 1,2$$
 (21)

we find the contrast ratio to be

Contrast Ratio = 
$$T_2/T_1$$
. (22)

 $I_1$  and  $I_2$  in (21) are obtained from (19) with  $\beta = \beta_1(x, y)$  and  $\beta_2(x, y)$ , respectively.

When the region of integration in (21) is the entire square, the contrast ratio is limited by the fact that the director is not everywhere parallel to the diagonal. The contrast ratio can be improved drastically by limiting the aperture to a smaller region over which the alignment is more nearly uniform. Fig. 15 illustrates this effect in the case of square apertures.

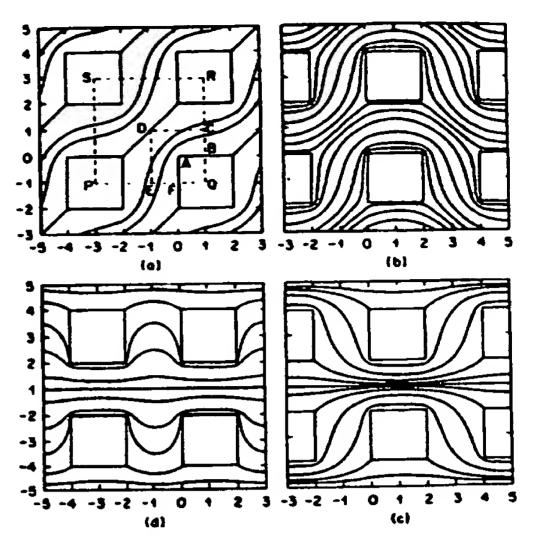


Fig. 16. Director lines in the region external to the squares of a periodic array of squares. Configuration (a) has the lowest energy. ABCDEF is the region in which Laplace's equation was solved. The patterns were then extended by symmetry.

Obviously reducing the aperture also reduces the brightness. Let us define a "transmission efficiency" as the ratio

Transmission Efficiency = 
$$\frac{T_2(\text{aperture})}{T_2(\text{entire square})_{\alpha=0}}$$
 (23)

For areas less than about 0.6 of the entire square, the transmission efficiency is essentially proportional to the area ratio, just as if the director were uniformly oriented.

#### V. PERIODIC ARRAYS

In order to make the elastic energy density comparable to or greater than the ubiquitous surface interaction energy, it is necessary to restrict the dimension of the square. In practice, a single display element may consist of a number of squares in an array. It becomes apparent that not only the interior of the squares, but the exterior defined by the array of squares may, in fact, have bistable states, electrically switched and optically differentiated as-already described. In a general sense, a periodic surface "lattice" with a particular set of symmetry properties may give rise to a corresponding set of local minima in elastic configurational energy. For example, a square array with  $C_4$  symmetry has two diagonal states while a triangular array with  $C_6$  symmetry has three.

Periodic arrays of squares, circles, or other shapes can be realized by means of posts, wells, or other topological patterns on one or both of the upper and lower surfaces.

The solution of Laplace's equation for the region exterior to an array of polygons with periodically repeated boundary conditions can be obtained by imagining partitions on which the boundary conditions can be deduced from symmetry. Typically, a closed cell can be formed whose boundaries are either walls along which  $\phi$  is known, planes of antisymmetry along which  $\phi$  is zero, or planes of symmetry along which its normal derivative is zero.

By this method, we have calculated the director line patterns shown in Fig. 16 for parallel boundary conditions at

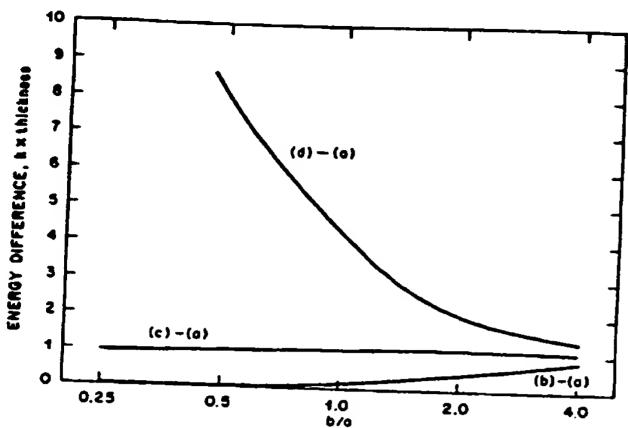


Fig. 17. Excess energy per unit cell *PQRS* of the configurations of Fig. 16(b) to (d) over that of 16(a) as a function of b/a. b = distance between squares. a = length of side of a square.

the edges of squares in an array. The different patterns result from different spatially periodic choices of "up" and "down" at the vertical boundaries. The configuration of lowest elastic energy is shown in Fig. 16(a), in which the director lines proceed diagonally through the lattice. Fig. 17 shows the energy excess of the other patterns as a function of b/a, where b is the distance between squares and a is the length of the edge of a square.

If the squares are rotated through 45° while keeping their centers on the same lattice, the configuration in which the director lines pass horizontally or vertically through the lattice (but still along the diagonals of the squares) is favored.

As with the internal states in a square, the realizability of bistability for an array depends on the existence of a sufficient energy barrier separating the minima. The discussions on the internal states of a square showed that the modal energy difference is small and probably insufficient to promote stability. The same is true of the external states. We must rely on the existence of higher order intermediate singular states to provide the needed barrier.

#### VI. CONCLUSIONS

We have described several two-dimensional structures exhibiting bistable states of liquid-crystal alignment. The topological distinction between them precludes continuous transitions between states, necessitating the creation or detachment of additional disclinations to achieve switching. This requires substantial activation energy which promotes stability in states that are not necessarily degenerate in energy, and provides for a possible energy threshold. When properly controlled, these processes could form the basis for a viable liquid-crystal display with memory.

At present, the vertical-horizontal bistable structures have shown greater promise. Experiments by Boyd, Cheng, and Ngo [2] have demonstrated reversible electrical switching in the alternating tilt bistable structure of Fig. 4 and the single tilt bistable structure of Fig. 2. One of the states in these experiments appears to be the horizontal state described here. The other has essentially all the optical properties of the planar vertical state, but evidence shows that a topologically equivalent largely vertical 180°-twisted state is, in fact, domi-

nant. With boundary tilt closer to the normal, the planar vertical state should be achieved unambiguously.

The necessity to detach and move disclinations is both an asset and a liability. While disclinations provide the basis for stability and a possible threshold, they also require higher voltages to achieve reasonable response times. Much can be done, however, to improve and optimize device performance.

The horizontal-horizontal structures offer greater variety. However, their implementation hinges on the achievement of a "slippery surface" on which liquid crystal-substrate interactions are reduced to a level insignificant vis-a-vis elastic energies. Investigations of this possibility are inconclusive at this stage.

Three-dimensional structures have not been treated here, although they may provide additional configurations combining the more desirable features of the two planar structures we have described.

## APPENDIX CALCULATION OF THE DIRECTOR FIELD

### A. Equilibrium Equation for Planar Configurations

The director orientation takes on that position dependence which, consistent with the constraints, minimizes the system energy. The elastic energy density g of a nematic liquid crystal is [29, eq. (3.15), p. 63]

$$g = \frac{1}{2}(k_1f_1 + k_2f_2 + k_3f_3) \tag{A1}$$

where

$$f_1 = (\nabla \cdot L)^2$$

$$f_2 = (L \cdot \text{curl } L)^2$$

$$f_3 = (L \times \text{curl } L)^2.$$
(A2)

Here L is the unit director of components  $L_x = \sin \theta \cos \phi$ ,  $L_y = \sin \theta \sin \phi$ ,  $L_z = \cos \theta$ , where  $\theta$  and  $\phi$  are the usual spherical polar coordinate angles, and  $k_1$ ,  $k_2$ , and  $k_3$  are the elastic constants for splay, twist, and bend, respectively.

To consider configurations in which the director lies in a plane, with the same orientation in parallel planes, we take  $\phi = 0$  and  $\theta = \theta(x, z)$  [vertical plane:  $L_x = \sin \theta$ ,  $L_y = 0$ ,  $L_z = \cos \theta$ ] or  $\theta = 90^\circ$  and  $\phi = \phi(x, y)$  [horizontal plane:  $L_x = \cos \phi$ ,  $L_y = \sin \phi$ ,  $L_z = 0$ ]. For such configurations, the twist function  $f_2$  vanishes.

The differential equations of equilibrium are obtained by minimizing the volume integral of g over the system. This results in the Euler equations [30, eq. (2.13), p. 277]. For the configuration in a vertical plane, the result is the following equation for the angle  $\theta(x, z)$  between the director and the z axis:

$$\nabla^{2}\theta + (1 - k_{1}/k_{3})[-\theta_{zz}\sin^{2}\theta - \theta_{xx}\cos^{2}\theta + \frac{1}{2}(\theta_{x}^{2} + 2\theta_{xz} - \theta_{z}^{2})\sin 2\theta + \theta_{x}\theta_{z}\cos 2\theta] = 0.$$
 (A3)

The subscripts on  $\theta$  indicate partial differentiation.

A tremendous simplification occurs when  $k_1 = k_3$  [13], for then (A3) reduces to Laplace's equation

$$\nabla^2 \theta = 0. \tag{A4}$$

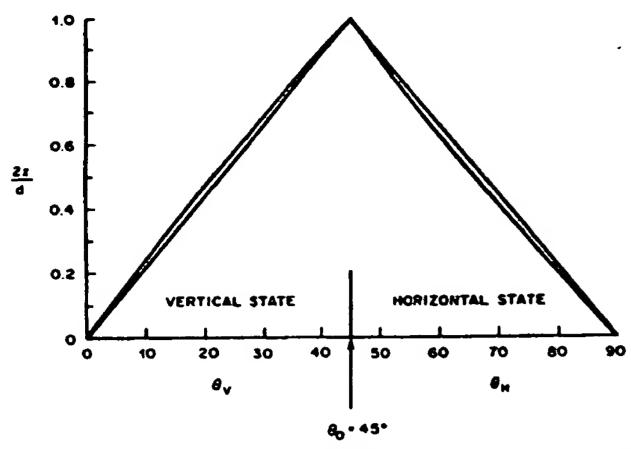


Fig. 18. Effect of  $k_1 \neq k_3$  on z dependence of director angle. The curves show director angle versus 2z/d for  $k_1 = k_3/2$  and the straight lines are for  $k_1 = k_3$ .  $\theta_H =$  horizontal state.  $\theta_V =$  vertical state. Boundary tilt  $\theta_0 = 45^\circ$ . Midplane of cell is at z = 0 and boundaries at  $z = \pm d/2$ .

For the (x, y) plane  $(\phi = \phi(x, y), L_z = 0)$  the simplification  $k_1 = k_3$  leads to  $\nabla^2 \phi = 0$ .

#### B. One-Dimensional Solution and Justification of Approximation $k_1 = k_3$

In the one-dimensional situation of Fig. 2(a) or (b),  $\theta$  depends only on z. From (A3), the equilibrium equation for  $\theta(z)$  is

$$\frac{d^2\theta}{dz^2} - (1 - k_1/k_3)(\theta_{zz} \sin^2 \theta + \theta_z^2 \sin \theta \cos \theta) = 0.$$
 (A5)

With leftward tilt at the boundary of magnitude  $\theta_0$ , the boundary conditions may be taken as

Fig. 3(a): 
$$\theta(-d/2) = \pi - \theta_0$$
,  $\theta(d/2) = \theta_0$   
Fig. 3(b):  $\theta(-d/2) = -\theta_0$ ,  $\theta(d/2) = \theta_0$ . (A6)

By transforming to  $\theta$  as the independent variable in (A5), we obtain the solution

$$z(\theta) = cE(\theta, \alpha) + z_0 \tag{A7}$$

where  $\sin^2 \alpha \equiv (1 - k_1/k_3)$ , c, and  $z_0$  are constants, and  $E(\theta, \alpha)$ is the elliptic integral of the second kind [31, eq. (17.2.9), p. 5891

$$E(\theta,\alpha) \equiv \int_0^\theta (1-\sin^2\alpha\sin^2u)^{1/2} du. \tag{A8}$$

The determination of the constants c and  $z_0$  for Fig. 2(a) and (b) gives, respectively,

$$\frac{2z(\theta)}{d} = \frac{E(\pi/2, \alpha) - E(\theta, \alpha)}{E(\pi/2, \alpha) - E(\theta_0, \alpha)} \text{ (horizontal state)}$$
 (A9)

$$\frac{2z(\theta)}{d} = \frac{E(\theta, \alpha)}{E(\theta_0, \alpha)} \text{ (vertical state)}.$$
 (A10)

When  $k_1 = k_3$ ,  $\alpha = 0$ , (A8) then gives  $E(\theta, 0) = \theta$  and (A10) and (A9) reduce to the straight lines (11) and (12).

Fig. 18 illustrates the excellence of the approximation

 $k_1 = k_3$  in this one-dimensional situation by comparing results from (A9) and (A10) for  $k_1/k_3 = \frac{1}{2}$  with the straight lines (11) and (12) obtained when  $k_1 = k_3$ . Nematic liquid crystals typically have  $k_1/k_3$  between  $\frac{1}{2}$  and 1. Since the effect of unequal elastic constants is so small, all of our further calculations will use the approximation of equal elastic constants  $k_1 = k_3$ . This is not merely a hypothetical idealization but an approximation that is useful and good.

As noted already, this approximation  $(k_1 = k_3)$  reduces the equation of equilibrium to Laplace's equation. This equation can be solved by the method of separation of variables [32] or boundary integral methods [33].

#### ACKNOWLEDGMENT

Some of the solutions of Laplace's equation were obtained by using a program package written by J. L. Blue [33]. Data for plotting the director lines was derived from the solutions of Laplace's equation by using the ordinary differential equation solver ODES written by N. L. Schryer [34]. The plots of director lines were made using the GR-Z graphical routines of R. A. Becker and J. M. Chambers [35]. It is a pleasure also to acknowledge helpful discussions with Prof. R. B. Meyer of Brandeis University and with D. W. Berreman.

#### REFERENCES

- [1] M. Schadt and W. Helfrich, "Voltage-dependent optical activity of a twisted nematic liquid crystal," Appl. Phys. Lett., vol. 18, pp. 127-128, 1971.
- [2] G. D. Boyd, J. Cheng, and P. D. T. Ngo, "Liquid crystal orientational bistability and nematic storage effects," Appl. Phys. Lett., vol. 36, pp. 556-558, 1980.
- [3] J. Cheng, G. D. Boyd, and P. D. T. Ngo, "Bistable configurations and nematic storage displays," in Proc. Int. Electron Devices Meet. (Washington, DC, 1979).
- [4] D. W. Berreman and W. R. Heffner, "New bistable liquid crystal twist cell," submitted to J. Appl. Phys. "New bistable cholesteric liquid crystal display," Appl. Phys. Lett., vol. 37, pp. 109-111, 1980.
- [5] W. Greubel, "Bistability behavior of texture in cholesteric liquid crystals in an electric field," Appl. Phys. Lett., vol. 25, pp. 5-7, 1974.
- [6] S. K. Kwok and Y. Liao, "Transient phenomena of relaxation from an electric-field-induced nematic phase to cholesteric phase," J. Appl. Phys., vol. 49, pp. 3970-3975, 1978.
- [7] E. P. Raynes, "Cholesteric texture and phase change effects," in Nonemissive Electrooptic Displays, A. R. Kmetz and F. K. von Willisen, Eds. New York: Plenum, 1976.
- [8] C. Tani, F. Ogawa, S. Naemura, T. Ueno, F. Saito, and O. Kogure, "Storage-type liquid crystal matrix display," in Proc. 1979 SID Int. Symp., pp. 114-115.
- [9] T. J. Scheffer, "Distorted twisted nematic liquid-crystal structures in zero field," J. Appl. Phys., vol. 49, pp. 5835-5842, 1978.
- [10] A. Miyaji, M. Yamaguchi, A. Toda, H. Mada, and S. Kobayashi, "Control and elimination of disclinations in twisted nematic liquid-crystal displays," IEEE Trans. Electron Devices, vol. ED-24, pp. 811-815, 1977.
- [11] G. Porte and J. P. Jadot, "A phase transition-like instability in static samples of twisted nematic liquid crystal when the surfaces induce tilted alignments," J. Phys., vol. 39, pp. 213-223, 1978.
- [12] C. Fraser, "Theoretical investigation of Fréedericksz transitions in twisted nematics with surface tilt," J. Phys. A, vol. 11, pp. 1439–1448, 1978.
- [13] F. C. Frank, "On the theory of liquid crystals," Discuss. Faraday *Soc.*, vol. 25, pp. 19–28, 1958, eq. (27), p. 26.
- [14] J. Cheng and G. D. Boyd, "The liquid-crystal alignment properties of photolithographic gratings," Appl. Phys. Lett., vol. 35, pp. <del>444</del>-446, 1979.
- [15] J. L. Janning, "Thin film surface orientation for liquid crystals," Appl. Phys. Lett., vol. 21, pp. 173-174, 1972.
- [16] G. D. Dixon, T. P. Brody, and W. A. Hester, "Alignment mecha-

nism in twisted nematic layers," Appl. Phys. Lett., vol. 24, pp. 47-49, 1974.

[17] W. Urbach, M. Boix, and E. Guyon, "Alignment of nematics and smectics on evaporated films," Appl. Phys. Lett., vol. 25, pp. 479-481, 1974.

[18] D. Meyerhofer, "New technique of aligning liquid crystals on surfaces," Appl. Phys. Lett., vol. 29, pp. 691-692, 1976.

[19] L. A. Goodman, J. T. McGinn, C. H. Anderson, and F. Digeronimo, "Topography of obliquely evaporated silicon oxide films and its essect on liquid crystal orientation," IEEE Trans. Electron Devices, vol. ED-24, pp. 795-804, 1977.

[20] R. Chabicovsky and G. Stangl, "A matrix addressed liquid crystal color display," in Conf. Rec. 1978 Biennial Display Research Conf. (Cherry Hill, NJ, Oct. 24-26, 1978). Library of Congress Catalog Card no. 78-51716.

[21] W. R. Heffner, D. W. Berreman, M. J. Sammon, and S. Meiboom, "Liquid crystal alignment on surfactant-treated obliquely evaporated surfaces," Appl. Phys. Lett., vol. 36, pp. 144-146, 1980. Also private communication concerning TiO2.

[22] D. W. Berreman, "Anomalous stiffness and tilt angle in nematics from nonuniform attachment angle," J. Phys. Colloque C3, vol. 40, suppl. no. 4, pp. 58-61, Apr. 1979.

[23] R. B. Meyer, "Alignment of liquid crystals by inhomogeneous surfaces," J. Phys., to be published.

[24] G. H. Heilmeier and L. A. Zanoni, "Guest-host interactions in nematic liquid crystals. A new electro-optic effect," Appl. Phys. Lett., vol. 13, pp. 90-91, 1968.

[25] D. L. White and G. N. Taylor, "New absorptive mode reflective liquid-crystal display device," J. Appl. Phys., vol. 45, pp. 47184723, 1974.

- [26] W. H. DeJeu, C. J. Gerritsma, P. VanZanten, and W. J. A. Goosens. "Relaxation of the dielectric constant and electrohydrodynamic instabilities in a liquid crystal," Phys. Lett., vol. 39A, pp. 355-356, 1972.
- [27] M. Born and E. Wolf, Principles of Optics, 3rd ed. New York: Pergamon, 1965.
- [28] D. C. Flanders, D. C. Shaver, and H. I. Smith, "Alignment of liquid crystals using submicrometer periodicity gratings," Appl. Phys. Lett., vol. 32, no. 10, pp. 597-598, 1978.

[29] P. G. deGennes, The Physics of Liquid Crystals. Oxford, England: Clarendon, reprinted 1975.

[30] P. M. Morse and H. Feshbach, Methods of Theoretical Physics. New York: McGraw-Hill, 1953.

[31] L. M. Milne-Thomson, in Handbook of Mathematical Functions. M. Abramovitz and I. A. Stegun, Eds. New York: Dover, Fifth Dover Printing, 1968, ch. 17.

[32] H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids. Oxford, England: Clarendon, 1959, pp. 166-167.

[33] J. L. Blue, "Boundary integral solutions of Laplace's equation," Bell Syst. Tech. J., vol. 57, pp. 2797-2822, 1978.

[34] N. L. Schryer, in PORT Mathematical Subroutine Library (a Bell Laboratories Proprietary Product Obtainable from Western Electric Company, Patent Licensing, P. O. Box 20046, Greensboro, N.C. 27420), P. A. Fox, Ed., 2nd ed., 1977.

[35] R. A. Becker and J. M. Chambers, "GRZ: A system of graphical subroutines for data analysis," in Proc. Computer Science and Statistics: 10th Ann. Symp. on the Interface, D. Hogben and D. W. Fife, Eds., NBS Special Pub. 503, Apr. 1977.

4

## Retention Characteristics of Hole-Injection-Type **EEPROM**

YUKIO FUKUDA AND HIDEO KODAMA

Abstract-The retention characteristics of FAMOS-type EEPROM using avalanche injection of holes for trass operation were analyzed. The avalanche-injected holes into the SiO2 gate oxide are likely to be trapped at the defects in the gate oxide before arriving at the floating gate. Some samples show that the threshold-voltage shift due to trapped holes versus the threshold voltage shift due to the total holes injected into the oxide comes up to 80 percent. The retention characteristics of trapped holes are poor. By detrapping these holes, the drain voltage of a FAMOS-type device is increased. The resultant acceleration of the unintentional writing due to the channel current-induced hot electrons may be a dominant factor in the retention characteristics.

#### I. INTRODUCTION

ECENTLY, ERASABLE and programmable ROM's (EPROM's) using the floating-gate avalanche-injection MOS (FAMOS) structure [1] have been widely used, particularly in conjunction with microprocessors and microcomput-

Manuscript received March 11, 1980; revised June 19, 1980.

The authors are with Musashino Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, 3-9-11, Midoricho, Musashino-shi, Tokyo, Japan.

While presently UV-erasable PROM's still dominate in most applications, electrically erasable PROM's (EEPROM's) have attracted considerable attention because of their easy erasing capability, on-board reprogrammability, and low package cost [2], [3].

EPROM's memory-retention characteristics have been reported in many papers [1], [3], [4]. In these studies, hightemperature storage has been generally used to evaluate the retention, with the exception of unintentional writing due to hot electrons during repeated reading [5]. The unintentional writing is accelerated at low temperature and in a high electric field [5].

The charge loss by thermal excitation or the information loss by unintentional writing are factors independently affecting retention characteristics.

This paper describes the factors affecting the retention characteristics of n-channel FAMOS-type EEPROM's using hole injection for erasure. A commercially available EEPROM was used as a test sample.

Holes injected into the SiO2 are likely to be trapped before

0018-9383/80/1100-2080\$00.75 © 1980 TEEE